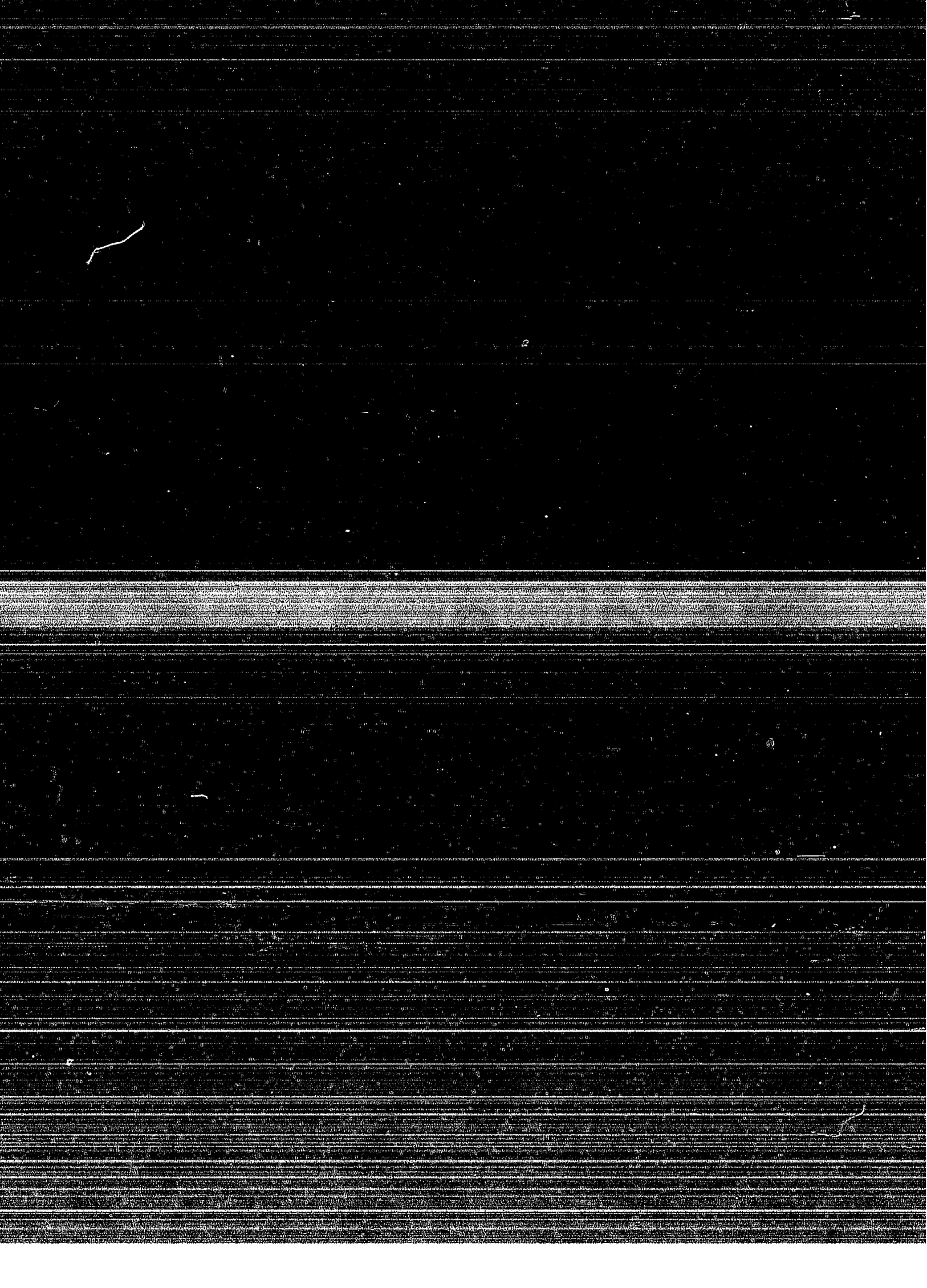

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

AN EVALUATION OF ALTERNATIVE TREATMENT METHODS FOR TRIHALOMETHANE REDUCTION IN PUBLIC WATER SUPPLIES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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Norman, Oklahoma

1984

AN EVALUATION OF ALTERNATIVE TREATMENT METHODS

FOR TRIHALOMETHANE REDUCTION

IN PUBLIC WATER SUPPLIES

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ACKNOWLEDGEMENTS

The work performed herein is the result of the assistance of a large number of people who gave unselfishly of their time and talents. My deepest appreciation is extended to Dr. James M. Robertson, Dissertation Committee Chairman, who was both patient and helpful during the course of this research. His friendship, guidance, assistance, and encouragement have been invaluable throughout my entire graduate program. I wish to express my appreciation to the other committee members, Dr. Jim F. Harp, Dr. Stanley C. Neely, Dr. Jerry Murphy, and Dan Guyer for the time and effort they were willing to invest in the successful completion of this project.

Special acknowledgements are also in order for all the assistance and encouragement given me by my co-workers and the administrative staff at the Oklahoma State Department of Health. Mark S. Coleman, Deputy Commissioner for Environmental Health Services, and Dr. Dwain Farley, Chief of General Environmental Services, supported the work and provided invaluable commentary on the subject of the dissertation. The personnel of the State Environmental Laboratory played a major role in the completion of this project, along with other personnel of the Oklahoma State Department of Health who assisted in the Lawton pilot study. Of particular importance in this pilot study were Joe Brown, Mike Daggett, Will Sasser, Mike Harrell, Johnny Taylor, Quang Pham, and Kay Coffey of the Oklahoma State Department of Health.

I express appreciation to Dr. Roy Deal of the College of Public Health whose patient instruction in Mathematical Statistics provided me the understanding needed to develop the statistical analysis contained herein.

I also express appreciation to my wife, Shelly, and to my children, Robert and Danielle for their support and understanding during the time spent in preparing this dissertation.

ABSTRACT

During the decade of the 1970's, much attention was focused on the presence of trihalomethanes in finished drinking water. One particular specie of the trihalomethanes, chloroform, was of particular concern due to this compound being a known carcinogen and due to it being, almost invariably, the predominant specie present in finished water. To date, the life-time exposure risk to this chemical as a carcinogen is uncertain. The Environmental Protection Agency (EPA) set a limit of 100 parts per billion (ppb) for total trihalomethanes (TTHMs) in finished water. This limit is based on an annual mean average of four quarters of sampling.

Compliance with this 100 ppb standard for TTHMs in finished water has prompted considerable research in the field of how TTHMs are formed, what factors relate to their formation, and remedial treatment in water treatment plants to reduce TTHM formation. This latter category of research has been extensive, but more often than not has dealt with testing of alternative treatment methods which would require either considerable capital outlay for additional treatment units (e.g. Granular Activated Carbon) or considerable increases in operating expenses (e.g. use of various coagulant-aid polymers), or both. Seldom has research in the area of remedial treatment considered the economic burden posed by implementation of these alternatives.

The objective of this research was to evaluate economically

feasible alternatives to reduce TTHM production in finished water. It has been well established by numerous researchers that the reduction of precursors (usually humic and fulvic acids) prior to chlorination can substantially reduce TTHM formation. Therefore, one alternative which would require minimal modification would be to chlorinate after coagulation-sedimentation rather than the usual practice of pre-chlorinating at the headworks of the plant. In conjunction with this, coagulant aids currently in use by a plant could be adjusted to optimize removal of precursors prior to mid-point chlorination as determined by jar-testing. A second alternative would be to simply optimize coagulation-sedimentation in order to reduce TTHM production in the distribution system. Thirdly, a cationic polymer could be used in place of the facilities' usual coagulant aid commensurate with optimized coagulation conditions of treatment. A fourth alternative would be to substitute pre-chloramination for pre-chlorination with optimized coagulation, while the fifth alternative would be to combine the use of a cationic polymer with pre-chloramination.

These five alternatives were tested in a pilot study at the Lawton Medicine Park Water Treatment Plant during mid-summer, the most critical time period for TTHM formation. It was desired to determine if (a) a significant difference existed between the alternative treatments, (b) which treatment alternative was most effective in controlling TTHM production, and (c) could critical period values be used to predict annual mean averages of TTHMs (i.e was there a

statistically significant correlation between the two variables?).

Analysis of Variance (AOV) was utilized to determine the most efficient treatment alternative. This test showed, with a high degree of reliability, that optimizing coagulation with existing coagulant aids in conjunction with pre-chloramination was the most efficient method for TTHM reduction. A regression analysis was then performed using TTHM data from 27 major Oklahoma water treatment plants across Oklahoma, all of which used surface water alone or in combination with ground water as their raw water source. This regression analysis indicated that a linear relationship exists between the TTHM values observed in the critical fourth quarter of the water year and the annual mean TTHM values, while a correlation coefficient of 0.91 and a t- test with a calculated t value well within the critical region of the curve gave further credence to the derived linear model for predicting the annual mean values of TTHMs from the critical period value. An experimental error term was applied to the linear model to correct for variance about the line of best fit. The model and error correction showed predicted values for the Lawton plant to be within 6 ppb of the annual mean average which could be expected by the percent reduction observed utilizing the preferred treatment method during the pilot study. The model and error correction were then utilized to predict annual mean TTHM values for the remaining 26 plants monitored. The final results showed that implementation of pre-chloramination in conjunction with optimized coagulation-sedimentation could be expected,

with 95% confidence, to reduce all 27 plants monitored to well below the annual mean TTHM maximum contaminant level of 100 ppb.

One significant aspect of these findings is that implementation of pre-chloramination combined with maintaining maximum coagulation conditions does not require elimination of post-chlorination. Therefore, a free chlorine residual can be maintained in the distribution system. Many facilities in this area of the country have completely substituted chlorination with chloramination. Research has shown that combined chlorine is not as effective in its bactericidal effect as free chlorine. A second significant aspect is that this research has demonstrated that the use of pre-chloramination can reduce annual TTHM means to below 100 ppb if used only during the critical period of the year when ambient temperatures and decaying detritus releasing precursors into the raw water source can cause peak TTHM production. This is not intended to imply that a water treatment plant should revert to pre-chlorination during the remaining nine months of the year. It is intended to imply that year-round operation using this treatment alternative provides a considerable margin of safety in assuring that the 100 ppb TTHM annual mean will not be exceeded.

In conclusion, this research has shown that relatively simple modifications in water treatment can achieve the desired result of reducing TTHM levels in order to bring many surface water treatment plants into compliance with state and federal regulations regarding

trihalomethanes. It is realized that for some water treatment facilities whose raw water source is extremely high in precursors, such simple modifications may not suffice. Nevertheless, this research has attempted to find economically reasonable treatment alternatives to reduce TTHM production and it is hoped that this contribution might offer many water suppliers guidance in achieving desired results with the least economic impact.

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CHAPTER I

INTRODUCTION

Much of the disease and mortality which have plagued civilized societies since the beginning of recorded history can be directly attributed to unsanitary living conditions. Particularly, the contamination of drinking water supplies is now known to have been the direct cause of the deaths of countless people over the centuries and has caused incalculable human suffering. The transmission of water-borne diseases by pathogens in impure water was, unfortunately, not recognized until the 19th century. Even then, both public ignorance and the lack of a safe disinfectant delayed any action to abate epidemics of water-borne diseases (1).

In the latter part of the 19th century in Europe, it was disovered that chlorine added to impure water in small quantities acted as a powerful bactericide. It was also discovered that a residual was

maintained in the water which gave lasting protection against recontamination. In the light of the times when water-borne pathogens were causing increased morbidity and mortality among growing centers of civilized society due to the industrial revolution, the discoveries of causative agents, mode of transmission, and chlorine as the remedy to stem the tide of death and human suffering was, without doubt, among the great discoveries of mankind.

The use of chlorine as a disinfectant in drinking water was initiated in Europe in the late 1800s and in the United States during the first quarter of the 20th century. By the 1930s, epidemics of water-borne diseases had been virtually eliminated in civilized nations.

The possibility of harmful effects of the addition of chlorine to drinking water was a secondary issue during the early 1900s, not only because of the far more urgent need to resolve bacteriological contamination, but also because of extremely limited knowledge as to the health effects of most chemicals and the ability to detect their presence with any accuracy. Even today, although our ability to detect the presence of chemicals has vastly improved, the acute and chronic health effects of many chemicals is theoretical at best. The first water quality standards for a limited number of chemicals was promulgated by the U. S. Public Health Service (USPHS) in 1914. These standards were not mandatory, in that the USPHS had no

constitutional authority to mandate standards. Many public water supply systems did, however, voluntarily adopt the recommended USPHS standards. In retrospect, one cannot avoid being stupified by the lack of a uniform set of enforceable drinking water standards in this country during the major part of this century.

It was not until 1969-1970 that public awareness of the poor quality of drinking water in this country was realized. This awareness was brought about by a massive study conducted by the Bureau of Water Hygiene (USPHS) of 969 water supplies serving over 18 million U. S. citizens (1). This study determined, in brief, that the quality of water being delivered to people across the country was far from satisfactory. Concurrently, the Federal Water Pollution Control Association (FWPCA) was conducting a study of organic chemicals in finished water from the City of New Orleans, Louisiana (2). This study revealed the presence of a large number of suspected carcinogens, one of which was chloroform.

With the formation of the U.S. Environmental Protection Agency (EPA) in 1972, one of the first objectives of the new federal agency was to investigate the findings of the FWPCA report on New Orleans drinking water. In a report released in 1972, EPA confirmed the FWPCA findings (2). Alarmed by their findings and due to public pressure exerted as the result of publicizing their findings, a second study was performed by the EPA on the New Orleans water supply and results were

again confirmed (3). One of the major concerns in these findings was the presence of trihalogenated methane compounds, the trihalomethanes (THMs). Studies being conducted by the International Agency for Cancer Research implicated one specie, chloroform, as a carcinogen (4). Meanwhile, J. J. Rook of the City of Rotterdam (Netherlands) had been researching the formation of trihalomethanes in drinking water and in 1974 published his findings that the reaction of chlorine with natural organic compounds (precursors) in the Rhine River caused their formation (5). In light of these newly developing facts, in November, 1974, EPA announced that it would conduct an 80-city survey of organics in drinking water. This study, the National Organics Reconnaisance Survey (NORS), showed the suspect carcinogen, chloroform, present in the finished drinking water of all cities practicing chlorination (6).

On December 16, 1974, the Safe Drinking Water Act (Public Law 93-523) was signed into law. Uniform standards of drinking water quality were established (7). The Act directed EPA to conduct an intensive study of public water supplies "to determine the nature, extent, source of, and means of control of contamination by chemicals or other substances suspected of being carcinogenic." This action resulted in the National Organics Monitoring Survey (NOMS) (8). This study confirmed the presence of THMs in every supply which practiced chlorination. On November 29, 1979, the National Interim Primary Drinking Water Regulation; Control of Trihalomethanes in Drinking Water; Final Rule, was published in the Federal Register (9). This

amendment established Maximum Contaminant Levels (MCLs) for Total Trihalomethanes (TTHMs), sampling frequencies, and provided for methods of compliance with regulations.

The key issue in the final regulation was that a time limit was set for compliance with the TTHM standard based on the number of people served by a particular water supply. Indirectly, it is the key issue of this dissertation in that the alternative treatment methods initially suggested by various groups and federal agencies would have, if implemented, been marginally effective (in retrospect) and cost prohibitive for many water supplies. That is, insufficient time was allowed by the final regulations to experimentally establish treatment efficacy by the proposed alternatives or to seek other equally efficient alternatives based on both efficacy and cost. Fortunately, the strong lobbying efforts of the American Water Works Association managed to slow the implementation process first suggested and gave researchers time to evaluate alternatives. Many of the initially suggested alternatives proved to be ineffective, while others proved to be only marginally effective with high operating costs.

This dissertation was, therefore, prompted by the need for such innovative research to evaluate, both by literature review and experimental analysis, the reduction of total trihalomethanes in finished drinking water based on simple modifications with minimal economic impact. It is hoped that the result of this effort will

assist public water supplies in making more effective management decisions in meeting the TTHM standards.

CHAPTER II

LITERATURE REVIEW

INTRODUCTION

The amount and quality of research conducted in the past ten years since the initial identification of trihalomethanes in finished drinking water on a national basis is astounding. The literature abounds with the findings of such research, including national EPA surveys, correlations between a variety of physical and chemical factors which influence the formation of trihalomethanes and remedial treatment alternatives to reduce TTHM levels in finished drinking water. Only in the area of human health effects of chronic exposure to the trihalomethanes is sound knowledge lacking.

This project will constitute a comprehensive review of the literature, particularly in regard to treatment methods used to reduce TTHM formation in the water treatment train and reduction of continued formation in distribution lines. Based on this literature review, the project will involve an on-line pilot study to evaluate various

treatment alternatives in order to determine the cost effective alternatives. In order to accomplish the literature review and subsequent experimental design decisions, it will be necessary to expand on the numerous factors and mechanisms which influence the formation and reduction removal of trihalomethanes. Such expansion on theoretical and empirical mechanisms will be included in the literature review.

While it is known that the predominant factor effecting the formation of TTHMs is the constituents in raw water, and in that waters vary dramatically in their physiochemical character from one area to another, the literature reflects a preponderance of commonalities from a technical/economic vantage. This review will, therefore, reflect those commonalities in order to establish common remedial alternatives.

The literature review will consist of Precursors and Mechanisms of Trihalomethanes Formation, Factors Influencing TTHM Formation, Alternative Treatment Methods, and Precursor Reduction Alternatives and Trihalomethane Reduction After Formation.

Precursors and Mechanisms of Trihalomethane Formation

It has been recognized since the studies by J. J. Rook in 1974 (5) and subsequent studies by numerous investigators, notably Bellar, Lichtenberg, and Kroner (10), that the formation of trihalomethanes is directly related to concentrations and types of precursors in the raw water source of a public water treatment facility.

Precursors referred to in trihalomethane formation are usually the naturally occurring organic compounds formed in surface water from decaying vegetation. The amount of precursors present in a raw water source may be manifested by color, representing the dissolved organics in the raw water. (Dissolved or suspended inorganic materials, manifested by raw water turbidity, do not appear to have any relationship to trihalomethane formation. Chemically, as will be discussed, inorganics would not be expected to affect THM formation). Precursors are most commonly fulvic and humic acids, though tannic acids and other organics may play a less significant role (11). Babcock and Singer (12) evaluated the relative importance of fulvic and humic acids in THM formation. While their study showed that humic acids are more efficient in THM formation than fulvic acids, a natural distribution of aquatic humus indicates that fulvic acids are far more prevalent then humic acids. Therefore, it can be stated with some credibility that in most surface water supplies the predominant precursor of interest is the fulvic acids. The point of interest in differentiation is that fulvic acids, with a molecular weight range of

100 to 1,000, are less easily removed in the coagulation-sedimentation process than are humic acids whose molecular weight normally exceeds 100,000.

The three major fractions of aquatic humus were first defined by Oden in 1919 (13), with structural models for humus proposed by Kleinhempel, et al. in recent years (14). The model is conceptualized as a large amorphous mass with functional groups protruding from its surface. The importance of the model is that these functional groups attached to the amorphous mass are the likely reaction sites by which, in the presence of chlorine, trihalomethanes are formed. In this respect, research has been done by a number of investigators as to the most effective functional groups in producing THMs. Rook showed in his studies, for example, that metahydroxy aromatic rings are particularly effective in producing THMs (15). In the traditional haloform reaction, the first ionization step is rate determining. Studies by Morris et al. (16) showed that functional groups of the humus mass are capable of executing this first inonization step rapidly. Further, in that the rate determining step in the haloform reaction is a hydrolysis reaction, Rook's observation of the importance of the metahydroxy aromatics would seem substantiated.

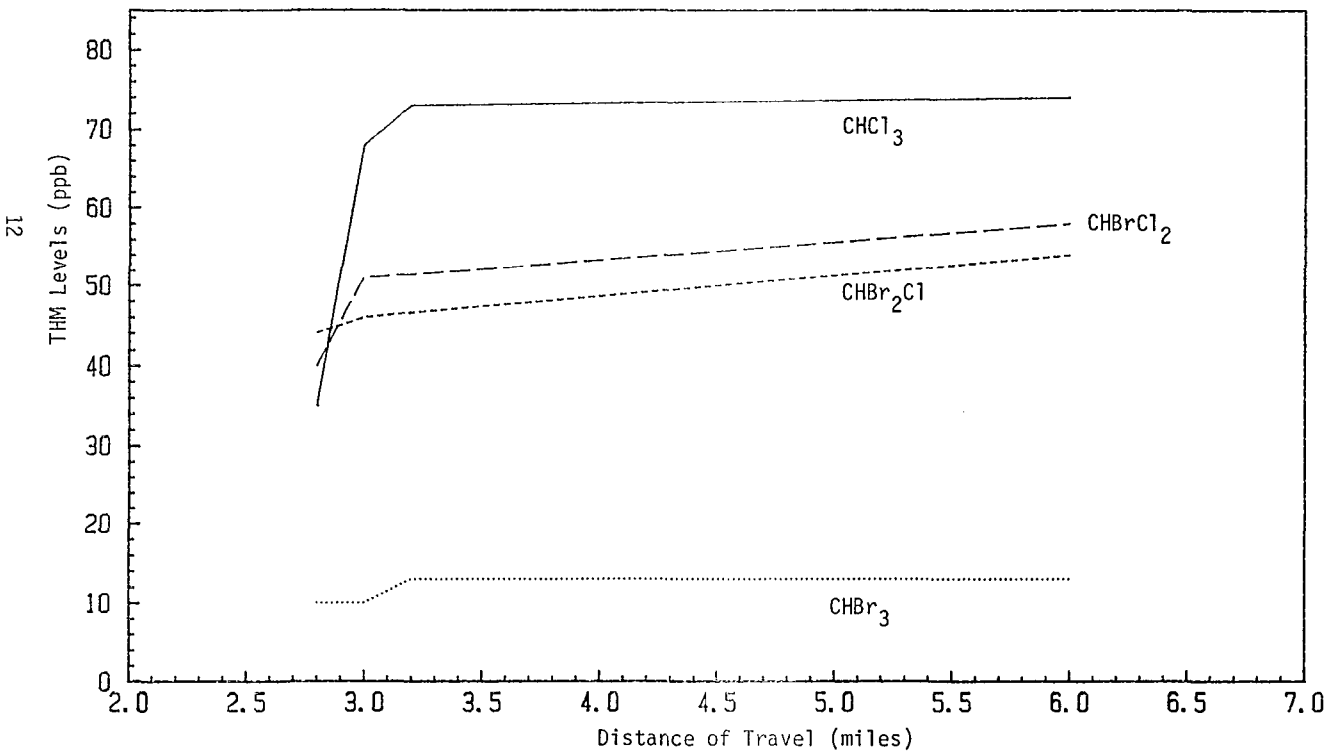
A further complication, from a water treatment viewpoint, is that the haloform reaction takes place over several hours with significant increases of THMs occurring even after 24 hours from

initial chlorine-precursor contact. It is this time of reaction that partially creates the problem of THM formation at distant points in the distribution system (Figure 1).

Although fulvic acid, due to a wider natural distribution, is recognized as the precursor of major concern, other precursors have been identified which are not related to hydrolysis in the haloform reaction. In a study performed by Lange and Kawczynski in the Sacramento-San Joaquin Delta (17), bromide was determined to be an important precursor in that, in the presence of chlorine, bromide is oxidized to form intermediates which apparently participate more effectively than chlorine in the halogenation step of THM formation. Another precursor group, the tannics, were identified by Telang et al. (18). This precursor group is of particular importance in areas where surface water runs through forrested areas in which clear cutting operations have been conducted.

The kinetics of the trihalomethane reaction are largely unknown. Numerous factors including pH, temperature, chlorine dosage rate, and precursor concentrations influence reaction rates. It is the nature and concentration of the precursor material present in a raw water source that specifically confounds the issue and makes it difficult to evaluate TTHM formation potential. However, it should be realized that TTHM formation potential has significance in the circumstance that a new raw water source is planned for utilization,

Figure 1. Plot of Formation of THM Species vs. Time of Travel



such as in the construction of a new water treatment plant, or in the planned use of an alternate source for an existing facility. In this event, utilization of total organic carbon measurements can normally predict whether a new raw water source is likely to produce TTHMs. The relationship is linear with a positive slope. In earlier research performed by the author, it was determined that such a linear relationship exists with a TOC value of 10 ppm being the approximate break-point at which the Maximum Contaminant Level (MCL) for TTHMs will likely be exceeded on an annual mean basis (i.e. if TOC values observed in the raw water source show a consistent pattern of exceeding 10 ppm, it is likely that some type of treatment method will be required to reduce TTHM formation) (19).

Factors Influencing Total Trihalomethane Formation

In order to evaluate the most effective and concurrently economical alternative treatment methods for reduction of trihalomethanes in finished drinking water, a literature search was performed pertaining to those factors which have a significant effect on the rate of TTHM formation.

Precursors

The most significant factor influencing formation of TTHMs, particularly in the water treatment train, is the type and concentration of precursors in the raw water supply. This factor has been discussed in the previous section.

Disinfectants

Although others exist, there are four commonly recognized disinfectants which are used in water treatment; chlorine, chlorine dioxide, ozone, and chloramines. Each of these disinfectants has profoundly differing effects and will be discussed separately.

Chlorine. Chlorine, either in the form of the dry powdered calcium hypochlorite or in the liquid form of sodium hypochlorite is the most commonly used disinfectant in water treatment facilities. Chlorine is highly effective in its bactericidal effect, its production of a free chlorine residual, and its aid in other treatment processes such as an oxidant to enhance coagulation efficiency and for removal of

iron and manganese, reduction or elimination of taste and odor problems, and control of algal growths in filter beds and sedimentation basins. These many benefits of chlorine make the consideration of an alternate disinfectant a difficult decision.

Due to the production of a free chlorine residual, chlorine is the disinfectant most associated with trihalomethane formation. Therefore, it would be beneficial to be able to quantitate the effect of chlorine (e.g. chlorine dosage). Unfortunately, much confusion exists in the literature regarding not only the influence of chlorine dosage rates on THM formation, but the rates of the reaction. Figure 2 illustrates the formation of TTHMs over time and resulting free and combined chlorine residuals (EPA). The first region of the diagram represents immediate chlorine demand, usually exerted by an inorganic demand due to sulfide, iron, and ammonia. There appears to be no relationship between the chlorine dose and THM formation during this initial phase. In the second region, when chlorine reacts with available organic material, a near linear relationship exists between chlorine dose and THM formation. Once the inorganic and organic demands are satisfied, a long-term chlorine residual is maintained with no further increase in THMs. (This latter fact will prove to be of critical importance in this research.) The EPA has also verified that long-term chlorine residuals result in only small to negligible increases in THM formation (20). Figure 3 would indicate that very little difference exists between a chlorine dose rate of 3 to 6 ppm,

Figure 2. Chloroform Formation By Free and Combined Residual (EPA)

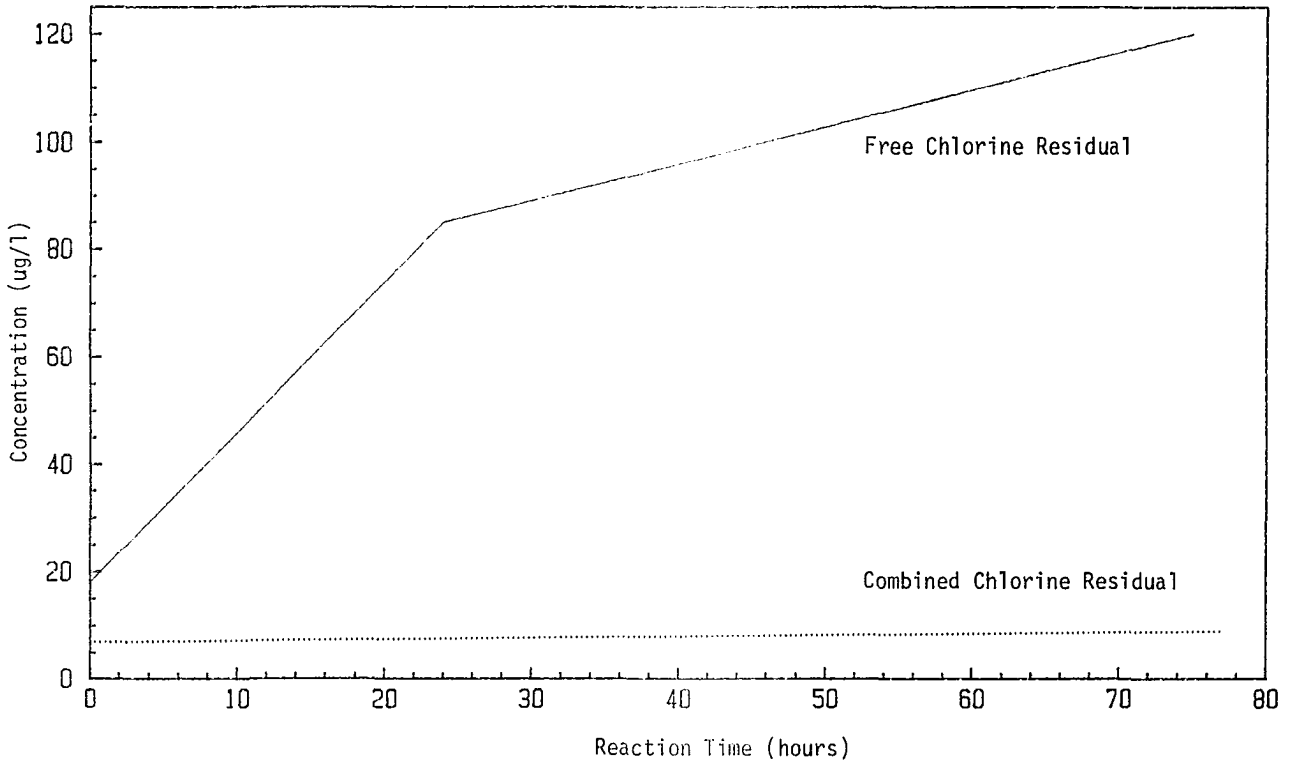
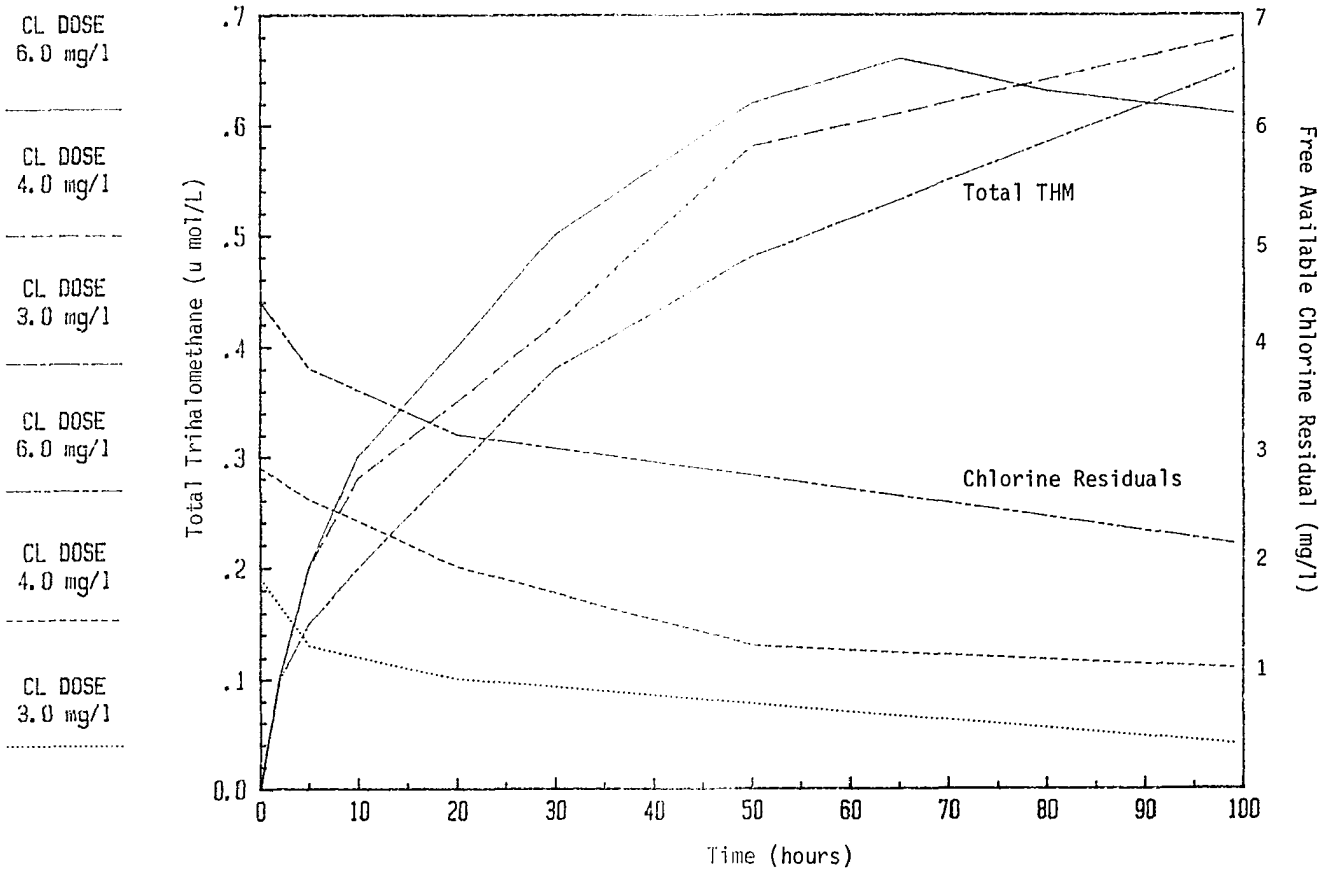


Figure 3. Effect of Chlorine Dose On TTHM Formation (EPA)



but that only at higher dose rates is a maximum of 0.2 ppm free chlorine residual maintained.

Chlorine Dioxide. Chlorine dioxide is a strong oxidant and disinfectant, but suffers three disadvantages. The use of chlorine dioxide is more costly and under certain conditions can form chlorite and chlorate ions which are injurious to health. Further, the use of chlorine dioxide can also cause production of chlorine as a by-product and, subsequently, trihalomethanes. The use of chlorine dioxide will be expanded upon in the next section.

Ozone. Ozone is a strong oxidant and does not form trihalomethanes. However, the use of ozone does not provide residual disinfection and is expensive to implement and operate. Additionally, as will be discussed later, dissociation of ozone produces hazardous organics which require removal by activated carbon.

Chloramines. Chloramines are formed as the result of the reaction of ammonia with chlorine. Chloramines are weak disinfectants, but do not produce trihalomethanes in that a combined, rather than a free chlorine residual is produced. Depending on the amount of chlorine added, three chloramines can be produced; monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3). The production of trichloramine occurs when too much chlorine is added per unit weight of ammonia. In that mono- and dichloramine are the active

disinfecting agents, the production of the trichloramines is not desirable.

pH

The haloform reaction is base-catalyzed. It would be expected, therefore, that the pH of the water in the treatment train would have a profound effect on THM formation. Figure 4 illustrates the relationship between pH and THM formation. Reduction of pH to near neutral conditions would appear to be an effective preventative measure in THM formation (EPA). This effect was verified by a study performed in Contra Costa County (California) which demonstrated a 50% reduction in THM formation by pH adjustment alone (17). Other researchers have determined that even in the absence of a free chlorine residual, THM formation occurs if the pH is raised. They attribute this phenomenon to formation of chlorinated intermediates at a low pH that hydrolyze to form THMs once the pH is raised (18).

Temperature

It would be expected that the temperature of treated water would be directly related to the rate of THM formation. Figure 5 shows this effect, demonstrating that THM formation nearly doubles between $3^{o}C$ and $25^{o}C$ (EPA). This factor must be taken into account, not because the ambient temperature of the raw water source is feasibly controllable, but because seasonal fluctuations must be taken into account when determining the most effective alternative treatment

Figure 4. Influence of pH On Chloroform Production (EPA)

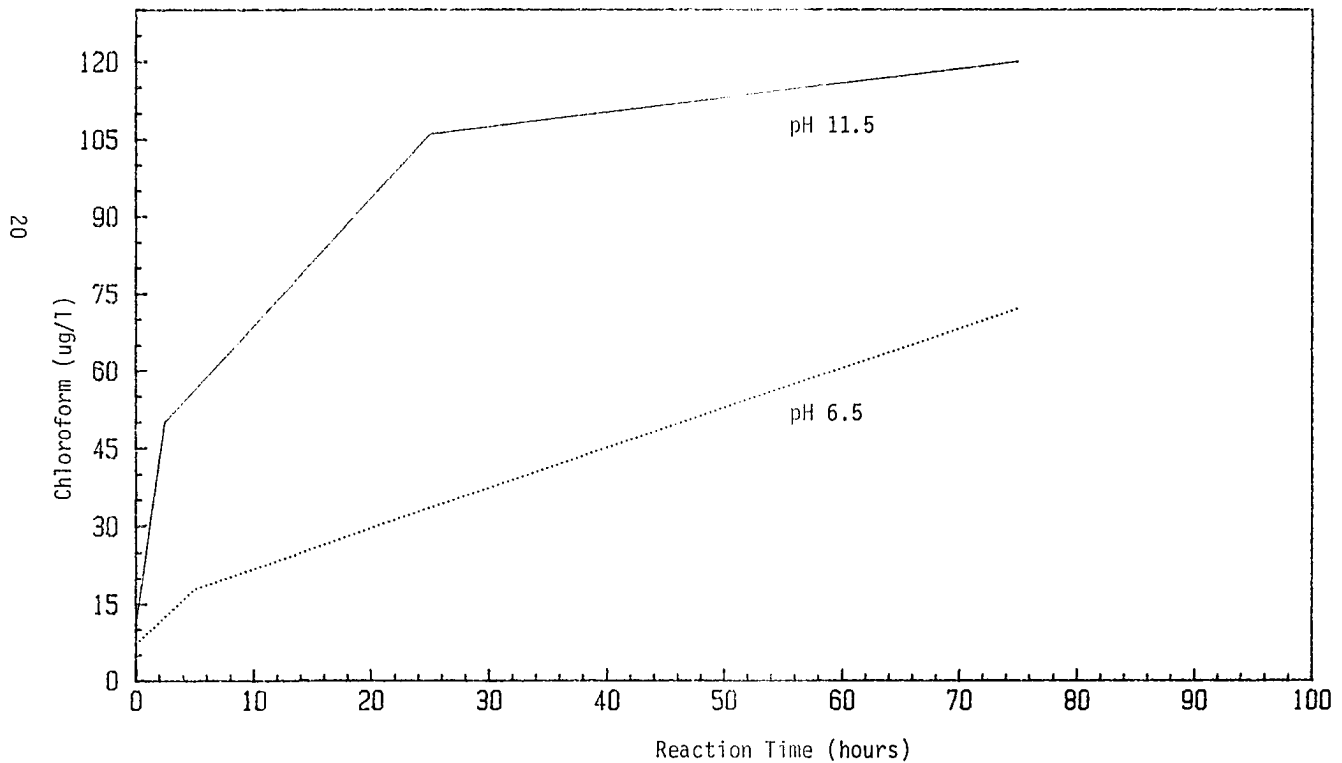
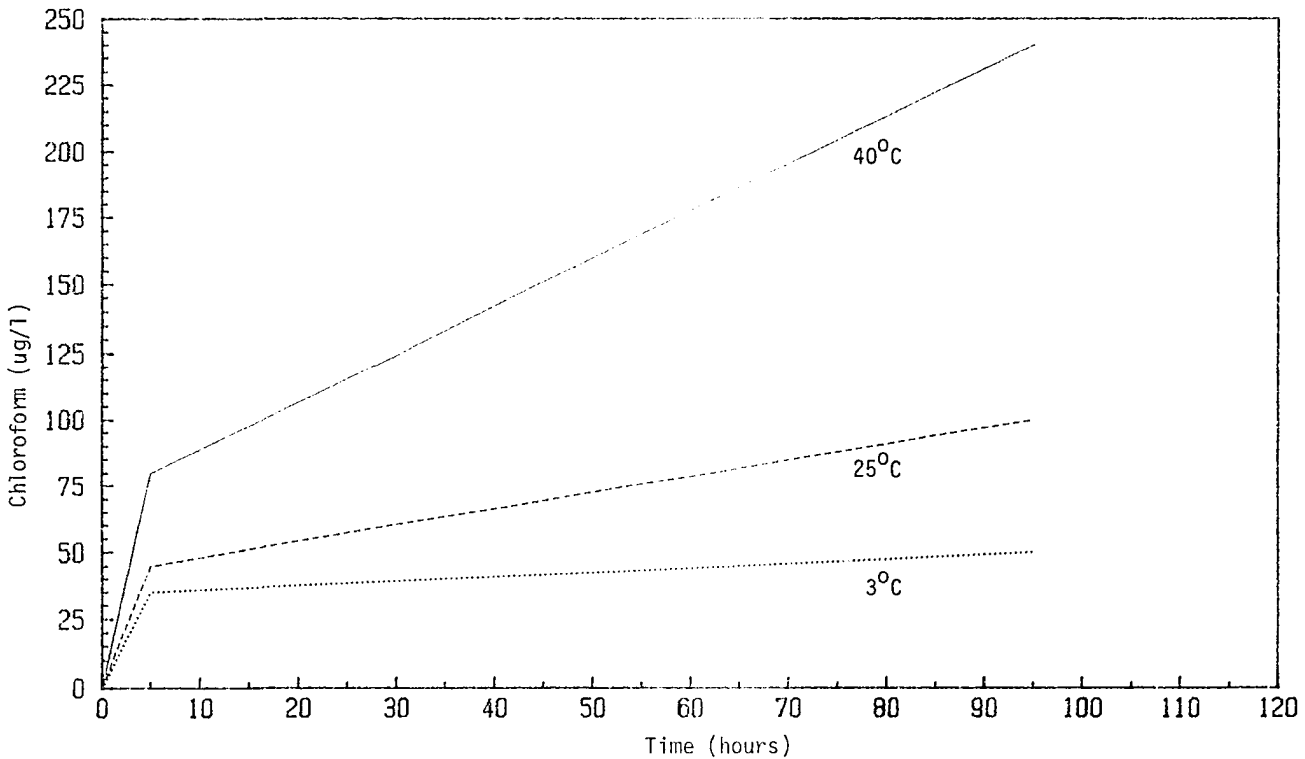


Figure 5. Influence of Temperature on THM Formation (Ohio River-EPA)



methods. (This factor was used in the conduct of this research in that the predictive model was based on sampling under high ambient temperature conditions.)

These factors do not, of course, exhaust the possibilities of all factors which might influence both rates and levels of THM formation. Rather, these factors are those of which the literature expresses the most knowledge. Reaction rates are likely the key to a better understanding of practical remedial measures needed to control and reduce THM formation. Due to the natural diversity of precursors, such an understanding may be difficult to achieve and, even if such is achieved, it may be difficult to extrapolate to a prediction of rates of formation for a highly diverse aquatic environment.

This portion of the literature review guided research efforts in that it was decided to conduct sampling during periods when the rate of formation of trihalomethanes was most likely to be highest (mid-summer). Also, a water treatment facility needed to be selected for the pilot study which showed stabilization of a free chlorine residual for the majority of the distribution system available for withdrawal.

Alternative Treatment Methods

In that this project had the primary purpose of evaluating alternative treatment methods for affecting the reduction of TTHMs in finished water, the majority of this review of the literature will be presented in this section of the dissertation.

Basically, there are five ways suggested by the literature to affect reduction of TTHMs: (a) use of disinfectants other than chlorine; (b) modification of chlorination practices; (c) utilization of a combination of disinfectants; (d) precursor reduction alternative; and, (e) reduction of trihalomethanes after their formation.

Use of Disinfectants Other Than Chlorine

As mentioned previously, there are primarily three disinfectants other than chlorine that could be potentially used in the water treatment process. These include chlorine dioxide, ozone, and chloramines.

Chlorine Dioxide. In the United States, chlorine dioxide is used primarily as treatment to control taste and odor problems and has limited usage as a disinfectant. In Oklahoma, of the known disinfectant practices at 163 surface water treatment facilities, 93 percent use chlorine (72 percent as gas, 11 percent as sodium hypochlorite, and 24 percent as calcium hypochlorite), while the remaining 7 percent use chlorine dioxide as their primary disinfectant

(Table A-1, Appendix). Of the plants using chlorine dioxide in Oklahoma, more than half use it to maintain a chlorine residual and control taste and odor. In Europe, chlorine dioxide is used extensively to maintain chlorine residuals, but most facilities utilizing this disinfectant are of small size (5).

Chlorine dioxide is more effective than chlorine as a disinfectant over a broader pH range due to the fact that ClO_2 does not hydrolyze in water. Further, unlike chlorine, chlorine dioxide does not produce THMs. The restricted usage of chlorine dioxide results from two major disadvantages; higher costs and potential health risks. Health risks, as assessed by the EPA, relate to the by-products resulting from the reaction of sodium chloride and chlorine or sodium hypochlorite (21). Chlorine dioxide is generated on-site, using solid sodium chlorite, in one of two ways:

a) $Cl_2 + H_2O \longrightarrow HOCl + HCl$

$HOCl + HCl + 2NaClO_2 \longrightarrow 2ClO_2 + NaCl + H_2O$

b) $NaOHCl + HCl \longrightarrow NaCl + HOCl$

$HCl + HOCl + 2NaClO_2 \longrightarrow 2ClO_2 + 2NaCl + H_2O$

In the course of these reactions, both the chlorite and chlorate ions are formed and apparently persist in the distribution system. The EPA review indicated uncertainty about the toxicity of

chlorine dioxide, but clearly demonstrated the toxicity of the associated anions (22). The effect of these two anions appears to be similar, if not identical, to the effect of the nitrite ion in the disease methemoglobinemia. The chlorite ion appears to be the primary concern. In studies performed by the EPA's Office of Resources and Development, the concentration of chlorite ions constituted nearly 50% of the residual chlorine dioxide after 23 hours contact time (22).

At the present time, the consensus of most researchers in the field is that the potential health risks associated with formation of chlorate and chlorite ions preclude its use as an alternate disinfectant (21). Its use in taste and odor control (particularly those resulting from phenolic compounds) have been shown to be highly effective, but the production of the chlorite ion should be substantially reduced by the addition of excess mineral acid (23).

Ozone. As with chlorine dioxide, ozone has limited usage in the United States, but is extensively used in Europe (24). The practice of disinfection by ozonation is not used in Oklahoma at this time.

The use of ozonation as the sole disinfectant practice has the obvious disadvantage that a residual is not produced. Its popularity as a water treatment method in Europe emanates from the many benefits derived, including primary (in-plant) disinfection, break-down of

sulfites and surfactants, precipitation of iron and manganese, removal of turbidity, and the oxidation of numerous organic compounds including those which produce color, taste, and odor (25).

Ozone generation may be accomplished by silent electric discharge in air or oxygen, by electrolysis of water, or by ultraviolet radiation of air or oxygen. The first alternative is generally the most utilized because of its higher generation efficiency. Ozone is generated by passing air or oxygen between electrodes separated by an air gap and a dielectric (usually glass) across which an alternating potential of approximately 15,000 volts is maintained. The generated ozone can be applied to the water being treated by numerous methods, the method used being dependent upon design criteria (25).

The formation of epoxides and organic peroxides, which are known to be health hazards, is strongly suggested by the dissociation of ozone (25). Other researchers have suggested an increased incidence of skin tumors in mice and an increased mutagenicity (Ames Test) resulting from ingestion of ozonated water (26), (27). The literature consistently concurs in the finding that, in the event that ozonation is utilized, the formation of unknown organic compounds, many of which might cause acute or chronic health effects, dictates the removal of such potential compounds by activated carbon (26). Furthermore, in that a residual disinfectant is not maintained, some type of chlorination would have to be utilized before delivery of finished

water to the distribution system. Ozone utilization could be considered, therefore, as an expensive alternative to pre-chlorination.

Chloramines. Surprisingly, the use of chloramination as a disinfection method is rarely used in the United States or in Europe. At the time of this research, it was not being used in Oklahoma. Chloramination as a disinfection process reached peak usage in the United States between 1929 and 1939, but was thereafter virtually eliminated due to both difficulties encountered in breakpoint chlorination (formation of NCl_3) and the difficulty in obtaining ammonia compounds after the outbreak of World War II.

As was discussed in the previous section, the combination of ammonia with chlorine produces three chloramines; mono-, di-, and trichloramine. Monochloramine is a more powerful disinfectant than dichloramine, while the NCl_3 specie has little or no disinfecting power. The production of trichloramine occurs at breakpoint chlorination which is dependent upon both chlorine-to-ammonia ratios (dose rates) and the pH of the treated water. The best disinfectants, monochloramine and dichloramine, are formed at a pH of 7.0 with a chlorine to ammonia feed ratio of approximately 4:1 on a weight for weight basis. Table 1 shows the chemical equilibrium between mono- and dichloramine and the pH dependency of this equilibrium. Table 2 shows various feed rates required to achieve the specified combined residuals based on flow.

Table 1. Monochloramine/Dichloramine Equilibria

$$2NH_2Cl + H^+ \rightleftarrows NH_4^+ + NHCl_2$$

pH	% as NH_2Cl
5	16
6	38
7	63
8	84
9	94

Reference: William H. Glaze, Ph.D., University of Texas at Dallas.

Table 2. Chlorine and Ammonia Feed Rates (lbs/day) To Achieve Specified Combined Residual

FLOW (mgd)	1.9 mg/l Cl_2	1.9 mg/l NH_3	2.0 mg/l Cl_2	2.0 mg/l NH_3	2.1 mg/l Cl_2	2.1 mg/l NH_3
4	63	16	67	17	70	18
6	95	24	100	25	105	26
8	127	32	134	34	140	35
10	159	40	167	42	175	44
15	238	59	250	63	263	66
20	317	79	334	83	350	88
25	396	99	417	104	420	105
30	476	119	500	125	525	131

Reference: William H. Glaze, Ph.D., University of Texas at Dallas.

The formation of monochloramine produces a combined chlorine residual in the distribution lines which, while not as powerful a disinfectant as free chlorine, does provide a high degree of protection. As is the case with ozone and chlorine dioxide, trihalomethanes are not produced by the use of chloramination (28).

Comparative Disinfectant Efficiency

The foregoing discussion brings to issue the initial and residual disinfecting power of these three disinfection alternatives. G. C. White (29) has determined the following ranking in order of decreasing efficiency:

$$\text{Ozone} > ClO_2 > HOCl > OCl^- > NHCl_2 > NH_2Cl$$

Note: There is disagreement in the literature as to whether mono- or dichloramines is the more powerful disinfectant.

Basically, disinfectant efficacy relates to two factors: oxidation potential and chemical dissociation. Not all chemicals with a high oxidation potential are good disinfectants, but germicidal activity is directly related to this phenomenon (30). The oxidative potential is related to the surface reaction which occurs when the molecule comes in contact with a microorganism, while dissociation relates to the ability of the molecule to penetrate and disrupt cellular integrity. Anions are poor disinfectants because of the

preclusion of approach and diffusion through the cell membranes. The three most effective germicides, ozone, chlorine dioxide, and hypochlorous acid, all have high oxidation potentials and are undissociated, while the chloramines, though dissociated, have a low oxidation potential. This low oxidation potential reduces the ability of the chloramines to completely inactivate pathogens or to prevent regrowth in distribution systems (30).

A second factor which must be taken into account in the consideration of alternate disinfectants is the comparative resistance of microorganisms to disinfection. White (29) provided a ranking in order of decreasing resistance, as follows:

protozoan cysts > enteroviruses > enteric bacteria

Research is currently underway to precisely determine disinfectant efficacy of various disinfectants, but is not yet available. Of particular concern are the polio virus, hepatitus virus, and the cysts of Entamoeba histolytica and Giardia lamblia (31).

It is apparent, from a search of the literature in regard to utilization of alternate disinfectants, that total substitution of ozone, chlorine dioxide, or chloramines for chlorine is a hazardous decision and one that would be made without scientific basis at this point in time. A more suitable alternative would be to either modify

the treatment process such that points of chlorination (in-plant) could be moved downstream of precursor removal and/or to use a combination of chlorine with an alternate disinfectant. It must be kept in mind that pre-disinfection is used primarily for the purpose of controlling algal growths in filter beds, in-flow lines, and sedimentation basins, and not for destruction of pathogens. Of the three alternate disinfectants which could be substituted for this purpose, only chloramination has not been shown to produce by-products which are health hazards.

Modification of Chlorination Practices

The literature reviewed does not extensively address the plausibility of modifying chlorination practices with respect to points of application. Basically, the theme of most studies was to move chlorination after a portion of precursor material had been removed. These studies showed reductions in trihalomethane formation, but did not account for anticipated difficulties associated with conventional plant operations such as reduced efficiency of coagulation, removal of taste and odor, filter bed and clarifier fouling, and the most critical issue of distribution line disinfection residuals.

It is difficult, in fact, to ferret out this information from the literature in that it is seldom addressed singularly, but rather utilized as an adjunct to some other pilot study issue. For example, the utilization of granular or powdered activated carbon in precursor reduction has been repeatedly studied and often the researcher will

have included moving the point of chlorination below the flash mix area or GAC fixed filter bed. In other studies that will be discussed and referenced later, the effects of oxidizing precursors frequently includes relocation of the point(s) of chlorination. However, the key concern in such studies was not to assess the simple process of movement of the chlorination point(s), but to assess the efficacy of oxidants, adsorbents, or coagulant aids. One of the objectives of this research was to contribute knowledge to that aspect singularly in that such research is lacking in the literature.

Utilization of a Combination of Disinfectants

As with modification of point(s) of chlorination, the literature does not show a great deal of research in the area of utilizing a combination of disinfectants. In particular, the use of chlorine and chloramines at various key points in the treatment train has not been well researched. As has been previously mentioned, the use of singular disinfectant alternatives has been extensively studied, but what would appear to be the most logical approach -- combinations of disinfectants -- has been neglected as a disinfectant alternative.

The role of disinfectant/oxidants in water treatment practices must be borne in mind:

1. Pre-chlorination is used for a variety of purposes, including the control of algae growth in filter beds and sedimentation basins, in the control of bio-fouling in

water lines from the raw water source to the water treatment plant, as an oxidant to assist in iron and manganese removal, to enhance coagulation efficiency, and to help control taste and odor problems.

2. Post-chlorination is used to ensure that chlorine residuals are maintained in the distribution system in order to provide protection against growth of bacterial slimes or recontamination of the finished water.

In utilizing some combination of disinfectants, then, it is necessary to bear in mind what disinfectants might replace chlorine or what other oxidants or coagulant aids might replace chlorine, or what disinfectant in post-chlorination might replace chlorine, and still achieve the best effluent water quality while reducing THM formation. Again, the literature is lacking in addressing these issues singularly and such issues constitute other objectives of this research.

Precursor Reduction Alternatives and Trihalomethane Reduction After Formation

The literature is replete in consideration of the utilization of reduction of precursors and other organics by activated carbon, either by Granular Activated Carbon (GAC) adsorption or by Powdered Activated Carbon (PAC) in the flash-mixing area. Less information is available on the efficacy of organics removal by synthetic carbonaceous adsorbents, ion exchange resins, and polymeric adsorbents. Rather than reiterate the efficacy of each treatment alternative, this section will attempt to compare removal efficacy based on a literature search.

Adsorption by Activated Carbon

Granular Activated Carbon (GAC). In recent years, GAC has been used for removal of trihalomethanes after their formation and for removal of precursor materials prior to chlorination. Rook (1965) determined in his studies that efficiencies of greater than 95% in trihalomethane removal were achieved over a three-week period, while Symons (1976) showed similar results in limited studies. However, numerous laboratory test studies and pilot-plant studies have shown that GAC performs poorly in the removal of humic substances and other organic matter present in the raw water source (12), (32), (33), (34). It would seem appropriate to review the findings of this research in order to present a working knowledge of the factors affecting the adsorption mechanisms of GAC.

GAC pore-size distribution appears to be one of the key factors affecting the adsorption process. Studies performed by Lee et al. (1981) at the University of Illinois evaluated this factor utilizing adsorption isotherm tests. The study was particularly informative in that pore-size distribution was evaluated both prior to and following coagulation in order to assess the effect of alum on adsorption (35). Their study showed that the adsorption capacity and the rate of uptake of humic substances increased as the molecular weight decreased, that pore volumes in pores with a radius of less than 70 Angstroms correlated with adsorption capacity of GAC for precursors with a molecular weight of less than 1,000, while pores with a radius of less than 40 Angstroms correlated with adsorption capacity of GAC for precursors with a molecular weight of greater than 50,000; and, that alum coagulation enhances adsorption capacity and the rate of uptake of GAC, thus increasing bed life, due to the aluminum ion causing the humic molecules to aggregate. This inverse relationship of carbon particle size to adsorption capacity of GAC was also reported by Weber et al. (36).

Other factors affecting GAC adsorption capacity were studied by McCreary and Shoeyink (37). Their studies indicated that higher phosphate cation concentrations reduce repulsive forces at the carbon surface. Black and Christman (38) demonstrated in their studies that a decreased pH causes aggregation of humic substances, thus increasing individual particle size and thereby enhancing carbon adsorption

capacity. These effects of a varying pH were elucidated by Schnitzer and Kodama (39). Their studies suggested that at a pH less than 4, fulvic acid behaves like an uncharged molecule. As the pH increases, attached functional groups are ionized to form a larger negative charge on the macromolecule. This ionization/increasing pH relationship is theoretically linear. Consistently, the literature shows that, as would be logically assumed, the adsorption capacity of GAC is directly related to any condition which effects the ionic charge on precursors or other substances in the raw water source prior to or following alum coagulation.

Oxidation of precursor material prior to GAC adsorption has also been investigated by a number of researchers. Wilson (40) investigated GAC adsorption of fulvic acids pre-oxidized with hydrogen peroxide. His findings suggested that pore exclusion of the organic molecules, resulting from oxidation, caused the empirical finding of a marked decrease in removal efficiency. Benedek (41), on the other hand, showed in a pilot study that no significant difference was observable as the result of precursor oxidation before GAC adsorption. Studies on the effects of pre-GAC ozonation have shown biodegradation of precursors and other organics was enhanced on GAC filters, presumably due to organics being rendered more biodegradable by ozonation. The literature suggests, therefore, that the effect of oxidizing precursors prior to GAC adsorption is not well understood and that various research findings are in conflict. One of the major

reasons for this conflict in findings is that the effects due to ozonation have not been delineated from the adsorption process. That is, while it is apparent that biodegradation of organics on the filter bed may be enhanced by oxidation of organic molecules to more biodegradable substances, it is also apparent that oxidation may cause pore exclusion in the filter bed and thus reduce surface area for organic carbon/microbial interaction. An EPA study attempted to make this delineation in a pilot study, concluding that ozonation enhanced the removal of organics in the raw water, but not necessarily by increasing bio-activity. Their study suggested that the interaction of particulate and dissolved organic matter may have been influenced by ozonation, thereby increasing filter efficiency. This study did not, however, clarify the issue of what factors are actually involved in affecting GAC adsorption capacity by oxidation.

The efficacy of removal of trihalomethanes or precursor materials by GAC fixed filters appears, from a search of the literature, to be somewhat in question. A preponderance of research has, however, demonstrated that GAC effectively removes THMs and other organic substances. What appears to be in question is efficacy which, by definition, implies more than short-term reduction at high operating costs. That is, few factors affecting the GAC adsorption process are understood and what is known is that many water treatment processes have adverse or enhancing actions on adsorption. It is also known that, regardless of attenuating actions, GAC filter

bed lives are short-term and the filter media must be replaced or reactivated frequently, causing high operating costs.

One of the more alarming aspects of the use of GAC filters in the water treatment process is the phenomenon of breakthrough or sloughing of accumulated intermediates from the filter bed. The practice of chlorination prior to GAC adsorption has been shown to have a significant effect on adsorption capacity in the upper levels of the filter bed, such effects including increased sulfur oxide production, increased hydrophilicity of the carbon, inhibition of biodegradation, and the decreased capacity in the upper bed causing deeper penetration of organics and earlier breakthrough (42). In a study of Philadelphia drinking water, Yohe et al. demonstrated that organics were actually increased by using GAC filters, particularly when pre-chlorination was practiced (42). The issue of desorption in GAC filter media is, from a public health viewpoint, probably the most critical concern in using such filters and, from a search of the literature at the time of this research, has received the least attention. It would be difficult to ascertain at precisely what point in time desorption begins, based on the variety of factors which influence breakthrough and such factors being infinitely variable depending on the type of water treatment and chemical character of the raw water source utilized.

Based on the technical research and the dirth of information on breakthrough products emanating from sloughing GAC filters, it is

the opinion of the author that the use of GAC filters for removal of precursors or THMs is not an acceptable alternative at the time of this research.

Powdered Activated Carbon (PAC). There has been limited research on the use of PAC as a treatment method for removal of precursor materials or trihalomethanes as the result of a "write-off" by the EPA in 1978 and 1979 (43) (44). This write-off resulted from two studies conducted by EPA which concluded that "unrealistically" high feed rates of PAC would be required to effectively reduce either precursor or THM levels. However, as was mentioned in the discussion of GAC adsorption, a number of factors influence the efficiency of carbon adsorption. Among these factors, it was noted that pore size was one of the more critical points. In the EPA studies, only one type of PAC was utilized, thus limiting the validity of their conclusion.

Optimization of PAC pore size for removal of target precursors and THMs was developed and tested at the Kanawha Valley water treatment plant in Charleston, West Virginia by Anderson et al. (45). This study demonstrated that this particular PAC formulation was highly effective at low feed rates in THM reduction, particularly when the point of chlorination was moved downstream of the carbon slurry application point. This would suggest that this PAC formulation is more effective in precursor removal than in THM removal, although the study concluded that the PAC formulation was effective in removal of both precursors

and THMs.

The major disadvantage of the use of any PAC formulation in THM reduction is that the carbon slurry must be disposed of with the backwash from filter beds. This presents the problem of more stringent containment of all backwash water in order to prevent leaching of adsorbents to groundwater. Furthermore, the literature does not show extensive testing of this alternative, thus it is difficult to evaluate a variety of research on this treatment technique in order to arrive at an unbiased conclusion. Therefore, at the time of this research it must be assumed that the usage of PAC formulation targeted for removal of precursors or THMs is not a feasible treatment alternative due to limited research and the unknown economic impacts of adding carbon feeders and adequate containment of filter backwash wastewater. Nevertheless, it is conceivable that the specially formulated PAC used in the referenced study may prove to be an effective alternative treatment method in the near future.

Synthetic Carbonaceous Absorbents (SCA). SCAs are formed by partial pyrolysis of macroporous polymer beads and have been tested in fixed filter beds as an alternative to GAC. The focus on one particular SCA, XE-340, manufactured by a Philadelphia firm, resulted from the finding that this adsorbent is particularly effective in removal of low molecular weight compounds associated with drinking water (e.g. di- and trichlorinated ethanes). The fundamental flaw in

all currently available SCAs is that they do not remove THM precursors and are only marginally effective in removal of chloroform, the predominant THM specie of concern in finished drinking water. SCAs are mentioned here only in a preclusive context in that they must be deemed not feasible as an alternative method for THM reduction.

Ion Exchange Resins. Raw water used in water supplies generally contains predominantly neutral and acidic organic species. Leenheer and Huffman (46) classified organic components of surface water into hydrophobic and hydrophilic fractions, further stratifying fractions as basic, neutral, or acid. Their classification supports the premise that the major organic content of raw water supplies consists of neutral and acidic species. Basic (cationic) exchange resins, for this reason, have been studied for efficacy in precursor removal.

Resins are classified as to weak-base or strong-base, with the usage of a particular type being dependent upon the pH of the raw water source. Weak base resins are commonly comprised of poly-acrylamide or phenol-formaldehyde matrices with secondary or tertiary amine functional groups which serve as ion exchange sites. Preloading of weak-base resins with acid is required for optimum ion exchange in that the pKs of the amine functional groups are generally outside the range of interest for water treatment (pH of approximately 6). Free-base forms (not preloaded) have been found to be much less effective than

the acid forms (46). Strong-base resins differ from weak-base resins in having quartenary amine functional groups which operate as anion exchange sites over a much broader pH range. It would seem that the logical assumption would be to exclusively utilize the strong-base resin. However, it also follows that the high exchange affinities exhibited by strong-base resins can cause concommitant difficulties with respect to regeneration. Nevertheless, various researchers have shown from 46% to 50% reduction in organic carbon from raw water sources using strong-base resin (47) (48). Therefore, strong-base resins appear to be an attractive alternative in precursor removal, but further research is needed in the area of regenerability and degree of fouling. The literature indicates that the basic imbroglio in regard to ion exchange resins is a trade-off between capacity and regenerability.

Polymeric Adsorbents. Polymeric adsorbents differ from ion exchange resins in their lack of ionic functional groups. The literature indicates that these adsorbents have performed exceedingly well at concentrating organic pollutants with subsequent desorption exceeding GAC (46) (49). That is, activated carbon usually shows higher adsorption capacities, but has a much lower measure of reversibility than does polymeric adsorbents. However, studies by Boening et al. (50) have shown that polymeric adsorbents show little promise in water treatment application in the context of this paper in that these adsorbents have insignificant capacity for humic substances

and even less capacity for chloroform. Statistical analysis of isotherm data of various adsorbents by Weber et al. (36) have also shown that polymeric adsorbents behave poorly in adsorption capacity for target precursor substances.

In summary, precursor removal by activated carbons, synthetic carbonaceous adsorbents, ion exchange resins, or polymeric adsorbents do not appear at the time of this research to be feasible measures for accomplishing the objective of reduction of TTHM reduction in finished drinking water. The reasons for this conclusion, based on a literature search regarding efficacy of treatment of these methods, are that, (a) the method is cost-prohibitive; and/or (b) the method has not been sufficiently proven in its capacity or reversibility (desorption); and/or (c) the method has been shown to be marginally effective in reducing precursors to preclude TTHM formation.

CHAPTER III

METHODS AND MATERIALS

PROGRAM DESCRIPTION

Numerous water treatment facilities in Oklahoma are currently attempting alternative treatment methods with the objective of reducing Total Trihalomethanes (TTHMs) in finished water to obtain compliance with the 100 part per billion TTHM primary drinking water standard throughout their distribution systems.

Since there are numerous suggested methodologies for accomplishing this objective, municipalities and rural water districts are often confronted with a confusing array of alternatives for TTHM reduction. These systems do not have adequate information as to the most cost effective treatment methods. They also lack the facilities or resources to determine treatment efficiency of alternative methods to reach a cost-effective decision.

The thrust of this research effort was to focus on alternative

treatment methods which might preclude the necessity for installation of relatively expensive reaction units for either precursor or TTHM removal (e.g. GAC or PAC). Based on a knowledge of the factors which are known to influence the rate of TTHM formation, combined with knowledge obtained from previous research on in-plant TTHM formation, the research was aimed at treatment train modifications which might just as effectively reduce the rate of TTHM formation within the plant and subsequently in the distribution system.

In order to accomplish this objective, it was necessary to design an experimental model which shed information on TTHM formation based on the use of numerous alternative treatment methods with the intent of determining the most efficient method. The experimental design included the following considerations:

1. To preclude complications presented by split flows, the old Medicine Park water plant (1939) was taken out of operation and only the new Medicine Park water plant (1969) was operated during the period of the study.
2. Chlorination and coagulation processes were altered in various ways to determine the efficiency of TTHM removal.
   A. Chlorination
      1. The point of in-plant chlorination was moved from the head of the plant to just ahead of the filters.

2. A combined chlorine residual utilizing chloramines throughout the treatment processes was used in place of free chlorine residuals to reduce in-plant TTHM formation.

3. Post-chlorination was kept constant in both the above alternatives in order to assure free chlorine residuals in the distribution system.

B. Coagulation Aids

1. The most effective dosages of currently used coagulant aids were determined by using jar tests.

2. These dosages were then applied on-line in the plant to determine their effect on TTHM reduction in the distribution system.

3. An alternative coagulant aid, Betz 1190 polymer, was jar-tested to determine its effective dosage and applied on-line in the plant to determine the effect of this alternate coagulant aid in reducing TTHMs. Literature had indicated Betz 1190 to be effective in removal of compounds in the molecular weight range of TTHM precursors.

Study Design

Based on theoretical considerations, the design of the

experiment was oriented toward defining the effects of chlorination and coagulation variables while maintaining a constant post-chlorination dosage rate to maintain a free chlorine residual in the distribution system. In order to accomplish this objective, the study design provided for division of the study into a five-phase experimental methodology to test one or more variables while maintaining one or more treatment processes constant. Based on data collected from various points in the distribution sytem, a single-factor Analysis of Variance could be performed using six treatments and five replicates. The five phases of experimentation consisted of the following:

Phase 1: Pre-chlorination was discontinued and mid-point chlorination was instituted. Coagulation aid dosages, predetermined by jar tests, were optimized and held constant throughout all five phases of the design.

Objective: To determine whether improved coagulation would reduce precursor levels in the raw water such that, in combination with moving the point of initial chlorination, a reduction in the level of formation of TTHMs in the plant and distribution system could be realized.

Phase 2: Pre-chlorination was reinstituted and mid-point chlorination was terminated while improved coagulation was held constant.

Objective: To differentiate between the effects of pre-

chlorination and mid-point chlorination while improved coagulation was held constant.

Phase 3: Pre-chloramination was tested as an alternative to pre-chlorination with chlorine gas. This was accomplished by the addition of ammonium sulfate in the flash mixing area immediately downstream of the chlorine gas injection point.

Objective: To determine whether the use of combined chlorine is as effective as free chlorine in controlling algae on filter beds and in sedimentation basins, while concurrently assessing levels of TTHM formation in the plant.

Phase 4: Pre-chloramination was discontinued and pre-chlorination was reinstituted. An alternate coagulant aid, a cationic polymer, was utilized in place of Cat-Floc A (Calgon).

Objective: To determine whether the use of an alternate coagulant aid could, in and of itself, reduce precursor levels sufficiently to significantly reduce TTHM levels in the plant and in the distribution lines.

Phase 5: Pre-chloramination was reinstituted. Cat-Floc A polymer (the usual cationic coagulant aid) was discontinued and Betz 1190 was substituted in its place.

Objective: To determine whether Betz 1190 acted more efficiently as a coagulant aid than Cat-Floc A in conjunction with pre-chloramination.

Field Sample Collection

The methodology of sample collection for THMs consisted of collection of samples in 40 milliliter test tubes sealed with teflon lined screw caps with a septum for sample withdrawal. Prior to field collection, the tubes and caps were heated at 200°C for two hours in order to remove trace contaminants which might produce interferences during analyses. A few grains of sodium thiosulfate were added to the tubes prior to sample collection. The samples were collected from points in the distribution system by adding five milliliters of sample to each tube. The tubes were shaken for several minutes to mix the water sample with the sodium thiosulfate. The sodium thiosulfate acts to prevent any further THM formation. Upon transport to the laboratory, iso-octane was added to each sample tube in order to extract the haloform fraction and an aliquot of 5 microliters was withdrawn by syringe. The five microliter aliquot was then injected directly into the port of a gas chromatograph for analysis.

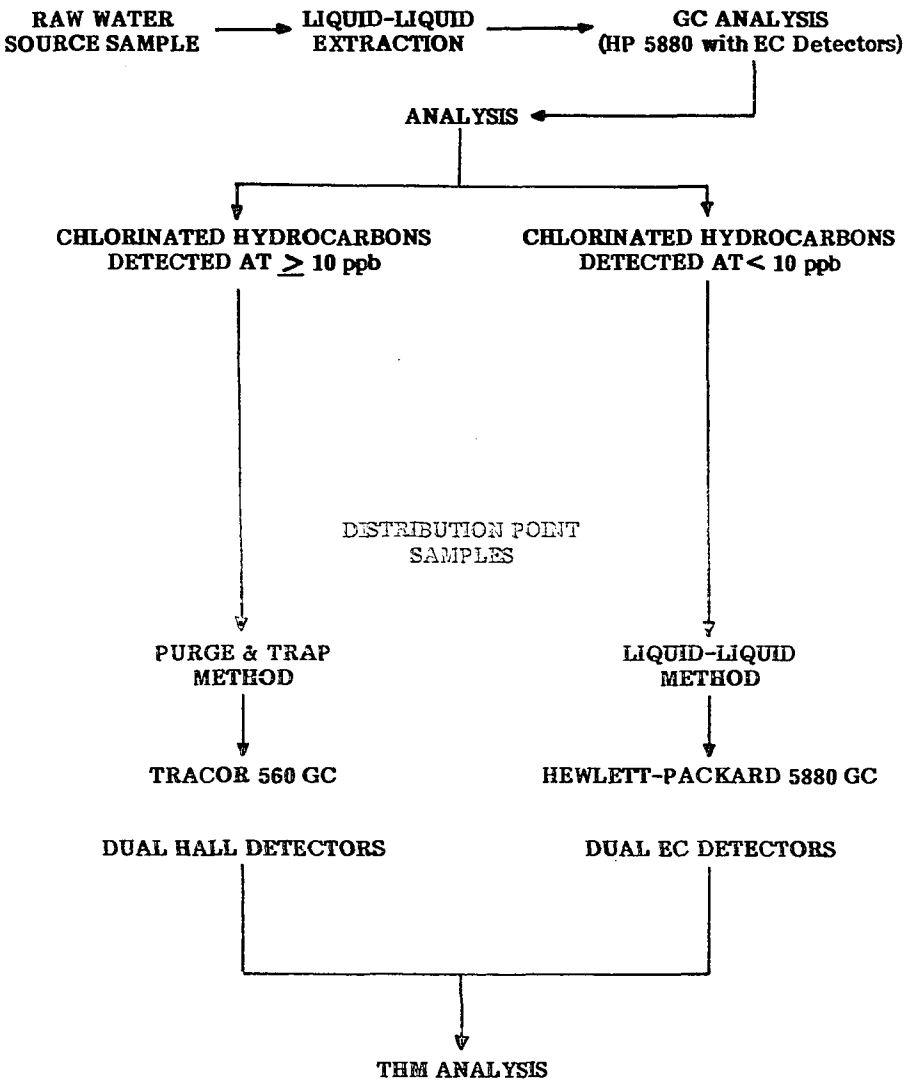
Sample Extractions and Analyses

Sample extraction procedures and analysis for trihalomethanes were taken from the Federal Register; Control of Trihalomethanes in Drinking water; Final Rule (Part III); November 29, 1979 (9).

Extraction Procedures. Before deciding upon the extraction method to be utilized, samples of the raw water sources were treated thusly:

1. Ten milliliters of sample were removed through the septum with a syringe and needle.
2. Into a vial, two milliliters of iso-octane were measured and a ten milliliter aliquot of sample was added giving a 5:1 dilution.
3. Vials were sealed with teflon-coated caps and inverted several time to extract THMs with iso-octane.
4. For each run, a set of not less than six standards of known concentrations between two and 300 ppb, one blank, and one spiked deionized water sample were prepared in methanol and extracted with iso-octane (Liquid-Liquid Extraction).
5. A five microliter aliquot of sample was injected, by direct injection, into a Hewlett-Packard 5880 Gas Chromatograph (GC) with dual Electron Capture (EC) Detectors. The purpose of this analysis was to determine if halogenated compounds (e.g. trichloroethylene) were present in the raw water source in sufficient concentrations (i.e. 10 ppb or greater) to cause interference in analysis using the liquid-liquid extraction method.
6. Figure 6 illustrates the mechanisms by which extraction and analysis methods determinations were made. In the event that halogenated compounds were detected in the raw water source, the purge and trap method was utilized with

Figure 6. Extraction and Analysis Method Determination



a Tracor 560 GC using Dual Hall Detectors. Hall Detectors are designed for specifically detecting halogens, while the purge and trap method increases sensitivity. In the event that the raw water source did not contain halogenated compounds, the liquid-liquid extraction method was used with a Hewlett-Packard 5880 GC using Dual EC Detectors.

Precise experimental procedures for the purge and trap method utilized were taken from Volume 44, Number 231 of the Federal Register, pages 68672-68682, and for the liquid-liquid extraction method from pages 68683-68689. The decision flow-chart is derived from the same Federal Register, Part II. 3, Interferences, page 68683. Figures 7 and 8 illustrate the Purge-Trap System in both the Purge-Sorb and Desorb Modes, respectively.

Figure 9 shows an actual run on one sample for trihalomethanes.

Analytical Quality Control

All analyses were performed for this research by the OSDH State Environmental Laboratory. The Laboratory is certified by the Environmental Protection Agency for monitoring public water supplies, including the analysis of trihalomethanes on an annual basis. The certification procedure includes on-site inspections by a team of EPA

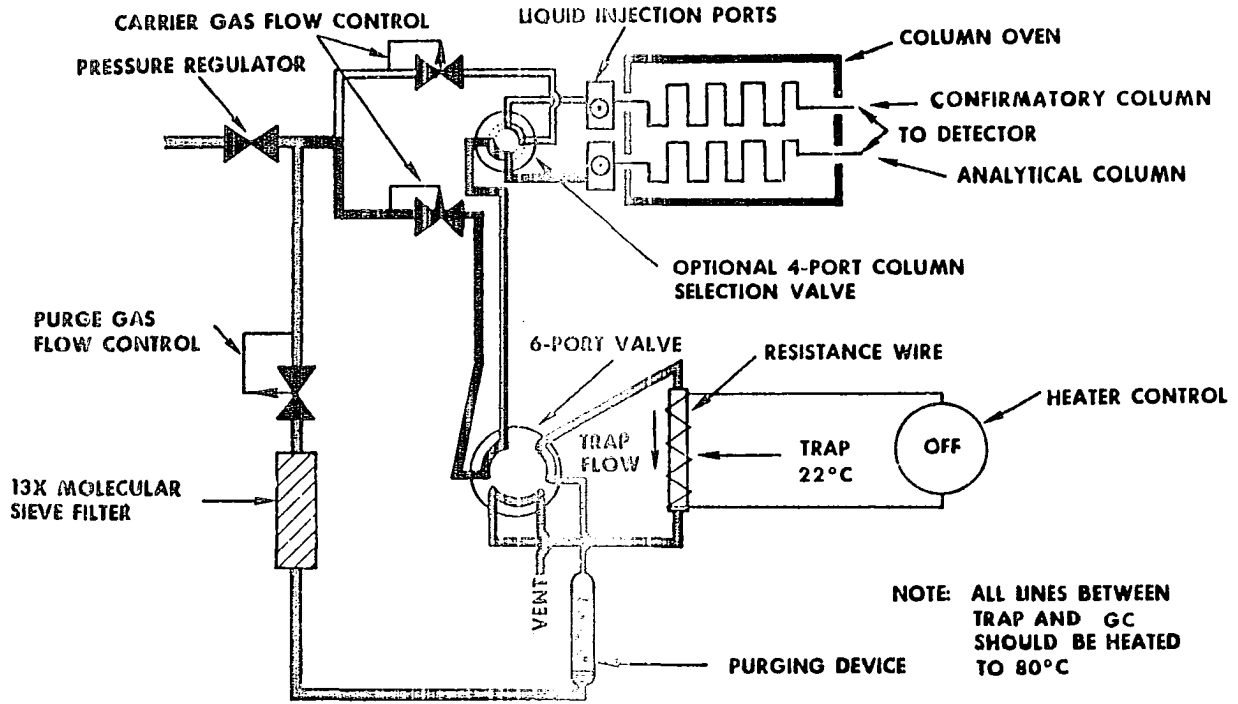


Figure 7. Purge-Trap System (Purge-Sorb Mode)

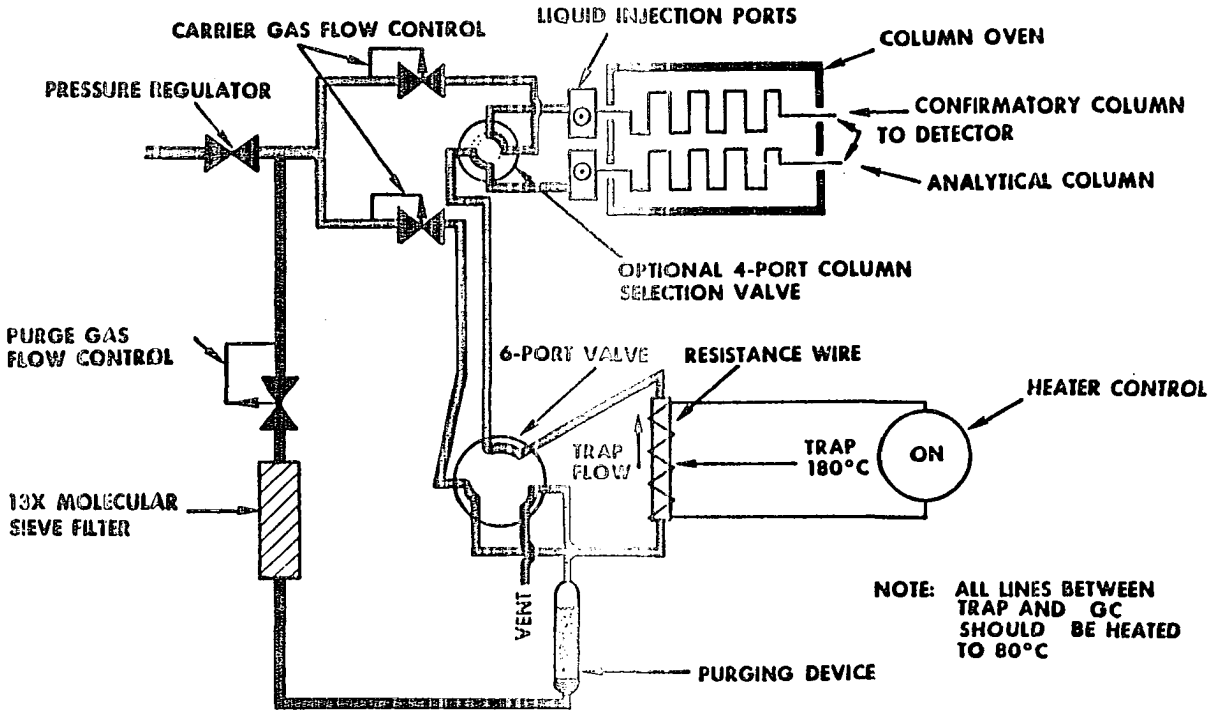
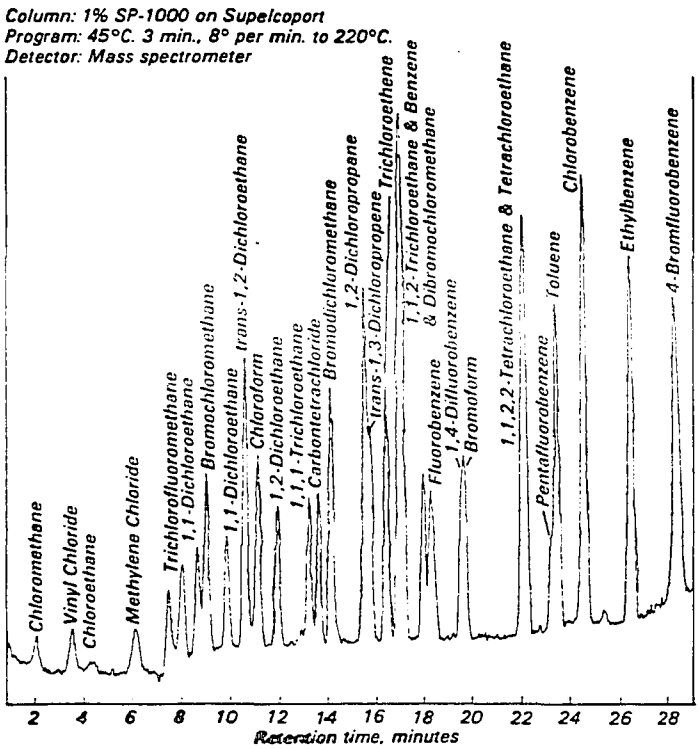


Figure 8. Purge-Trap System (Desorb Mode)

Figure 9. Gas Chromatograph of Volatile Organics



technical personnel, inter-laboratory quality assurance check samples and intra-laboratory procedures of quality assurance including spiking, sample recovery, replicate sample analysis, and reference standards.

THM analyses were run in sets of ten. Each set of ten samples included one duplicate, two spiked samples for precision and percent recovery, and one reference standard. A set of reference standards, a minimum of six, in concentrations ranging from two to 300 ppb were run at the beginning of each day. Precision of analyses was determined by the difference of the two spiked samples concentrations. The accuracy of the test was determined by percent recovery.

Completed data were utilized to plot QA charts to insure that tests were in control.

CHAPTER IV

RESULTS AND DISCUSSION

INTRODUCTION

The objective of this research project was to determine whether selected alternative treatment methods in the production of finished drinking water might effectively reduce levels of formation of trihalomethanes to below the 100 ppb Maximum Contaminant Level (MCL) on an annual mean basis. In order to accomplish this objective, it was first necessary to select that quarter of the year during which observed data from numerous water treatment facilities in Oklahoma showed the highest levels of TTHMs. Table 3 shows that of the 27 facilities monitored, 26 showed the highest levels of TTHMs during the fourth quarter of the Water Year (July through September). These facilities were not randomly selected. They are facilities which (a) utilize surface water alone or in conjunction with ground water as their raw water source; and, (b) serve populations of 10,000 or more persons. Sampling criteria which would produce data conducive to the stated objective included, in addition to sampling during the most critical time frame, selection of a facility at which the TTHM

Table 3. Total Trihalomethane Levels for 27 Water Treatment Facilities in Oklahoma, By Quarter

Facility Name	Jul-Sep 4th Quarter	Oct-Dec 1st Quarter	Jan-Mar 2nd Quarter	Apr-Jun 3rd Quarter	Annual Mean
Altus	113	68	90	97	92
Ardmore	89	73	52	42	64
Bartlesville	231	98	80	140	137
Broken Arrow	207	77	105	97	122
Chickasha	179	39	57	46	80
Claremore	147	47	53	60	77
Clinton	147	101	87	97	108
Del City	211	57	99	61	107
Duncan	173	102	84	106	116
Durant	54	50	56	70	58
Guthrie	298	88	149	98	158
Lawton	249	50	51	39	97
McAlester	291	98	34	108	133
Midwest City	114	80	65	52	78
Muskogee	319	55	78	165	154
Norman	225	67	77	113	121
OKC-Draper	127	86	74	24	78
OKC-Hefner	159	92	38	35	81
OSU-Stillwater	132	34	29	42	59
Okmulgee	136	38	54	40	67
O.O.W.A.	72	66	58	40	59
Ponca City	73	32	17	25	37
P.V.I.A.	227	61	83	71	111
Sand Springs	284	153	122	141	175
Shawnee	169	87	78	85	105
Tulsa-A.B. Jewell	132	55	54	42	71
Tulsa-Mohawk	50	22	13	21	27

formation curve neared stabilization at a minimum of five sampling points. If this could be realized, the five sampling points could be treated as replicates in an analysis of variance statistical test. Since the TTHM curve is time dependent as previously shown, it was necessary to make curve stabilization determinations prior to initiation of research. The Lawton Medicine Park Facility, due to its distance from the first point of withdrawal (approximately 10 miles) and medium range treatment capacity (14-15 MGD) showed a TTHM formation slope of near zero throughout the in-town distribution system. The research for this project was, therefore, conducted at the Lawton Water Treatment Plant. The AOV test was utilized to measure six treatment methods with five replicates per treatment. Predictions as to the annual mean TTHM, based on percent reduction determined in the pilot study, at the 27 water treatment facilities monitored during this research project were calculated based on a linear regression model. Both the AOV and regression analysis will be discussed in the statistical analysis section of this chapter.

Experimental Design

In attempting to resolve the problem of TTHM formation in finished drinking water systems, an experimental design should take into account the essence of the problem and attempt to preclude or circumvent the formation of TTHMs, not remedy the after-fact. In the short history of dealing with reduction of trihalomethanes in finished drinking water, much attention was initially focused on the use of

remedial action after THMs had been formed. For example, the use of GAC and aeration were both proposed and are reportedly highly effective in TTHM removal. However, initial capital outlay for both remedial measures is high and GAC must be thermally reactivated or replaced on a frequent basis adding approximately 15% to operational costs. Based on a more economically sound approach, much study on the reason for TTHM formation has revealed that numerous factors which have a profound effect on TTHM formation can be controlled by simple treatment modifications which do not require as large a capital outlay and can be implemented in a relatively simple manner.

The factors which can have a significant effect on TTHM reduction are highly dependent on the physical and chemical quality of a particular raw water source. Therefore, the experimental design should initially take into account the more feasible factors. Generally, alternatives include: (a) use of disinfectants other than chlorine; (b) modification of chlorination practices; (c) utilizing a combination of disinfectants; (d) removal of precursors prior to disinfection; (e) pH adjustment; (f) improved coagulation-clarification to more effectively remove precursors either by optimizing dosages or using other, potentially more effective, coagulant aids; and, (g) removal of precursors prior to chlorination by using Activated Carbon. The use of PAC or GAC is expensive and should be considered only as a last resort. While pH adjustment has been proven highly effective in reducing TTHM formation in that the haloform reaction is base-

catalyzed, the use of this alternative is highly dependent on the buffering capacity of the raw water. Furthermore, it is not desirable to deliver finished water to the consumer that might be corrosive. Therefore, this alternative should not be discarded, but reviewed with the chemical quality of the raw water source in mind. Removal of TTHMs after their formation, as has been mentioned, is expensive and does not preclude continued haloform reactions in the distribution system.

Having avoided the more costly or less expedient alternatives for this particular water source, several preventative methods remained available for trial. First, the study was performed during the summer season when ambient temperatures of the raw water were higher in that, as in many chemical reactions, there is a direct relationship between temperature and reaction rates. Since the drinking water standard is based on an annual mean of four seasonal samplings, it was felt that reduction of TTHMs during the summer season would be more recognizable and that projections of meeting the annual average MAL based on various alternatives could be more reasonably made. Secondly, it is recognized that other disinfectants do not react as strongly as does chlorine with precursors to form TTHMs. Therefore, the use of chloramines as a pre-disinfectant could be attempted, ammonium sulfate being one of the less expensive compounds for this alternative method. Thirdly, the point of pre-chlorination could be moved from the head of the plant to the filter influent point. Post-chlorination could be continued as a constant throughout the study to assure a free chlorine residual in the

distribution system, whether the point of pre-chlorination were moved or the use of chloramines was instituted. Post-chloramination was not utilized in that removal efficiency was realized, but is an additional possibility. Fourthly, the dosage of coagulation-sedimentation aids could be optimized to more effectively remove precursors. Fifthly, the use of other coagulant aids could be utilized to determine whether they were more effective in precursor removal and subsequent TTHM formation.

In summary, the theoretical considerations for this pilot study included: (a) more effective removal of reactive precursor material while introducing the highly reactive chlorine gas; (b) moving the point of pre-chlorination downstream from coagulation-clarification to attempt precursor removal prior to chlorination with chlorine gas while maintaining the filter and basins free of algae; and, (c) utilizing pre-chloramination in place of pre-chlorination in that chloramines do not react as readily with precursors as does free chlorine.

It should be emphasized that any experimental design for modifying treatment methods to reduce TTHM levels in a distribution system should first take into account the chemical and physical quality of the raw water source, since the nature of TTHM formation is highly dependent on this factor. In this sense, it might be assumed that no single method of alternative treatment will necessarily be applicable to any two systems. Nevertheless, based on theoretical considerations

of TTHM formation and empirical evidence of on-line effects, it is highly probable that one or more generalities can be derived and projected to achieve similar results for similar raw water sources. The realization of this probability was the major impetus for performing the Lawton Pilot Study.

Results of the Lawton Pilot Study

The Lawton Medicine Park plant draws water from Lake Lawtonka which is supplemented during low inflow periods by water from Lake Ellsworth. The Medicine Park facility consists of two separate, but similar plants; one built in 1932 and the other built in 1967. During the course of this study, only the newer plant was utilized in order to avoid complications presented by split flows. A flow diagram of the Lawton Medicine Park Facility is shown in Appendix A, page 107.

The Medicine Park facility basically utilizes pre-chlorination with chlorine gas; ferric sulfate, Cat-Floc A polymer, and slaked lime as coagulation-clarification aids; filtration; and post-chlorination at the 42-inch effluent line using chlorine gas. During the study, the facility treated between 14 and 15 MGD. Finished water is pumped to the City of Lawton with the first point of withdrawal being approximately ten miles from the plant and the most distant point being approximately 18 miles on the south side of the city.

The study was conducted in five modes (not counting the normal

operation mode) to determine whether optimizing coagulation-clarification aid dosages, altering coagulation aids, moving the chlorination point from the head of the plant to the filter influent, utilizing pre-chloramination in place of pre-chlorination, or some combination of these treatment alternatives could most effectively reduce TTHM formation in the distribution system.

Each alternative treatment method attempted caused TTHM reductions in the Lawton water distribution system (Table 4). Both from historical data and from base-line data acquired prior to initiation of the pilot study, June 28, 1982, it is evident that current water treatment practices at the Medicine Park Treatment Facility cannot reduce TTHM levels sufficiently to meet trihalomethane maximum allowable levels of 100 ppb as an annual average. Method II, Table 4, shows that the distribution line average TTHM can be reduced substantially by moving the point of chlorination to just before the filters and increasing the dosage rates of ferric sulfate, Cat-Floc A, and slaked lime to maximum clarification efficiency based on jar-testing. This approximate 32% reduction (Table 5) in TTHM formation in the distribution lines is most likely the result of a greater removal of precursor material during coagulation-sedimentation prior to chlorination, thus reducing the TTHM formation potential within the plant. Both chloroform and dichlorobromomethane showed erratic values initially which began to conform to a more uniform reduction throughout the system by the third day after initiation of this second alternative treatment method. Erratic values were likely the result of

Table 4. Trihalomethane Levels (ppb), Pilot Study at Lawton, Oklahoma

Treatment Method I (Normal Operations) June 28

Site	Chloroform	Dichlorobromo Methane	Dibromochloro Methane	Bromoform	Total THMs
1	132	51	14	< 2	197
2	155	55	14	< 2	224
3	134	53	14	< 2	201
4	138	54	16	< 2	208
5	130	50	17	< 2	197

Treatment Method II (Midpoint Chlorination; Optimized Coagulation) June 28 - July 2

Site	Chloroform	Dichlorobromo Methane	Dibromochloro Methane	Bromoform	Total THMs
1	69	37	14	< 2	120
2	50	40	15	< 2	105
3	70	39	15	< 2	122
4	168	59	16	< 2	178
5	128	50	16	< 2	177

Treatment Method III (Optimized Coagulation Only) July 3-5, July 9-13, July 15-18

Site	Chloroform	Dichlorobromo Methane	Dibromochloro Methane	Bromoform	Total THMs
1	125	48	12	< 2	185
2	127	51	13	< 2	191
3	110	43	13	< 2	166
4	118	45	11	< 2	174
5	135	49	13	< 2	197

Treatment Method IV (Prechloramination, Optimized Coagulation) July 6-7

Site	Chloroform	Dichlorobromo Methane	Dibromochloro Methane	Bromoform	Total THMs
1	43	23	8	< 2	74
2	36	14	4	< 2	54
3	37	15	4	< 2	56
4	23	8	2	< 2	33
5	27	12	3	< 2	42

Table 4. (continued)

Treatment Method V (Betz 1190 Polymer; Optimized Coagulation) July 7-8

Site	Chloroform	Dichlorobromo Methane	Dibromochloro Methane	Bromoform	Total THMs
1	120	48	13	< 2	181
2	162	55	14	< 2	231
3	148	51	13	< 2	214
4	122	49	13	< 2	184
5	156	54	13	< 2	225

Treatment Method VI (Betz 1190; Prechloramination; Optimized Coagulation) July 14-18

Site	Chloroform	Dichlorobromo Methane	Dibromochloro Methane	Bromoform	Total THMs
1	81	30	8	< 2	119
2	90	30	8	< 2	128
3	91	38	10	< 2	139
4	71	30	8	< 2	109
5	82	31	8	< 2	121

Site	Distance from Source
1	10-11 miles
2	11-12 miles
3	12-13 miles
4	13-16 miles
5	16-18 miles

Table 5. Observed Average Reduction in TTHM Levels Using Alternative Treatment Methods

	Method of Treatment	% Reduction
I.	Prechlorination using normal coagulation aid dosages	Base-line
II.	Mid-point chlorination using optimized coagulation	32%
III.	Optimized coagulation only	11%
IV.	Pre-chloramination using optimized coagulation aid dosages	75%
V.	Betz 1190 Polymer; Optimized coagulation	No significant difference
VI.	Betz 1190 Polymer; Prechloramination; Optimized coagulation	40%

Increased clarification aid dosages used during study were maximized as follows:

Ferric Sulfate	25.0 ppm
Cat-Floc A	2.0 ppm
Slaked Lime	10.0 ppm

uncontrollable variables relating to non-uniform water usage at points in the distribution system. However, based on long-term usage of this alternative method of treatment, an overall reduction of approximately 32% in TTHM formation could be anticipated. Relating this reduction to projected TTHM reductions, midpoint chlorination and increased clarification would not be sufficient to reduce the annual average TTHM values in the distribution system to meet the 100 ppb TTHM standard.

Method III of the study conducted from July 3 through July 6, July 7 through July 13, and July 15 through July 18, determined that the use of optimized dosages of coagulation-clarification aids caused an average TTHM reduction in the distribution system of approximately 11%. This reduction in TTHM formation can be assumed to be the result of a reduction in precursors reacting with chlorine during post-chlorination in that the only factor altered was improved coagulation. This would appear to substantiate other studies that in-plant formation of trihalomethanes is significant in the eventual formation of TTHMs in distribution lines. Method III further showed that the percent reduction of this method would not be sufficient to reduce the annual average TTHM values in the distribution system to meet the annual mean TTHM standard.

Method IV of the study, from July 6 through July 7, determined that the use of pre-chloramination in combination with increased dosages of coagulation-clarification aids caused a significant

reduction in TTHM levels in the distribution lines of approximately 75%. This reduction in TTHM formation in the distribution lines could likely be attributed to the fact that combined chlorine does not react as readily with precursors as does free chlorine. Since post-chlorination was continued throughout the study, this lends further credence to the concept that in-plant TTHM formation is one of the prime considerations in reducing TTHM formations in the distribution system. Furthermore, this method of treatment was determined to be the most effective in reducing average TTHM levels in the distribution system.

Method V of the study was instituted from July 7 through July 8, substituting Betz 1190 Polymer for Cat-Floc A to determine whether Betz polymer was a more efficient coagulant-aid than Cat-Floc A. Pre-chlorination was reinstituted in place of pre-chloramination with other increased dosages of clarification aids maintained. TTHM data from the distribution lines demonstrated that Betz 1190 Polymer was slightly less effective than Cat-Floc A as a coagulant-aid with no significant difference observed in THM levels.

Method VI of the study was instituted from July 14 through July 15 to determine whether the use of Betz 1190 Polymer in combination with pre-chloramination was more effective than the use of Cat-Floc A with pre-chloramination. Comparing data from Method IV, it was evidenced that there was no significant difference in the use of

Betz 1190 Polymer vs. Cat-Floc A polymer as a coagulation aid, with both methods showed reductions in average TTHM levels in the distribution system sufficient to meet TTHM standards. Table 5 shows, however, that Method VI produced only a 40% reduction in TTHM levels as compared to a 75% reduction observed using Method IV.

Statistical Analysis

Introduction

The objective of this two part statistical analysis was first to determine the optimal treatment method by use of analysis of variance. Of the six treatment methods utilized, a significant difference was determined between Treatments IV and VI and all other treatment methods. No significant difference was determined between Treatments IV and VI. Treatment IV was considered to be the best treatment method based on the lower cost of Cat-Floc A used in Treatment IV compared to the higher cost of Betz 1190 polymer used in Treatment VI. Having established this, the next objective was to determine whether TTHM values in the July-September quarter showed statistically significant correlation with the annual mean TTHM. Having shown evidence of correlation between the two variables, it was then the objective to define the behavior of this correlation by developing a linear model for prediction purposes. Before using the linear model, the additional precaution of performing a t test using a hypothesis test was performed. This test further substantiated that the linear model developed by regression analysis was a reliable predictor.

Analysis of Variance

The initial statistical evaluation of the data generated as a result of the Lawton Medicine Park Pilot Study required a determination of whether a significant difference existed between the treatment

methods utilized and, if so, which treatment method or methods could be shown to be significantly different from other methods with the objective of making a decision as to the most effective treatment method in reducing production of total trihalomethanes in the distribution system.

The statistical approach utilized was a single-factor analysis of variance (AOV). The calculations for this statistical approach are as follows:

Table 6. Treatments and Replicates

Treatment	Replicate 1	2	3	4	5	Row Total, T_i	Row Mean, $\bar{x}_i$
I	197	224	201	208	197	1027	205
II	120	105	122	178	177	702	140
III	185	191	166	174	197	913	183
IV	74	54	56	33	42	259	52
V	181	231	214	184	225	1035	207
VI	119	128	139	109	121	616	123
Column Σ	876	933	898	886	959	4559	

$$SS(Total) = \Sigma (x^2) - \frac{(\Sigma x)^2}{n} \qquad n = 30$$

$$\Sigma (x^2) = 197^2 + 224^2 + \ldots + 121^2$$

	ck
= 38,809 + 50,176 + 40,401 + 43,264 + 38,809	211,459
= 14,400 + 11,025 + 14,884 + 31,684 + 31,329	103,322
= 34,225 + 36,481 + 27,556 + 30,276 + 38,809	167,347
= 5,476 + 2,916 + 3,136 + 1,089 + 1,764	14,381
= 32,761 + 53,361 + 45,796 + 33,856 + 50,625	216,399
= 14,161 + 16,384 + 19,321 + 11,881 + 14,641	76,388

ck 139,832 + 170,343 + 151,094 + 152,050 + 175,977 = 789,296

$$\Sigma (x^2) = 789,296$$

$$\Sigma(x^2) = (Ti)^2 = (4{,}552)^2 = 20{,}720{,}704$$

$$SS(TOTAL) = 789{,}296 - \frac{20{,}720{,}704}{30}$$

$$= 98{,}606$$

$$SS(FACTOR) = \frac{\Sigma(Ti^2)}{c} - \frac{(\Sigma x)^2}{n}$$

where c = number of replicates for each treatment

$$\Sigma(Ti^2) = 1027^2 + 702^2 + \ldots + 616^2$$

$$= 1{,}054{,}729 + 492{,}804 + 833{,}569 + 67{,}081 + 1{,}071{,}225 + 379{,}456$$

$$= 3{,}899{,}584$$

$$SS(FACTOR) = \frac{3{,}899{,}584}{5} - \frac{20{,}720{,}704}{30}$$

$$= 89{,}227$$

$$SS(ERROR) = \Sigma(x^2) - \frac{\Sigma(Ti^2)}{c}$$

$$= 789{,}296 - 779{,}917$$

$$= 9{,}379$$

Table 7. AOV Table

Source	SS	df	MS
Factor	89,227	5	17,845
Error	9,379	24	391
Total	98,606	29	

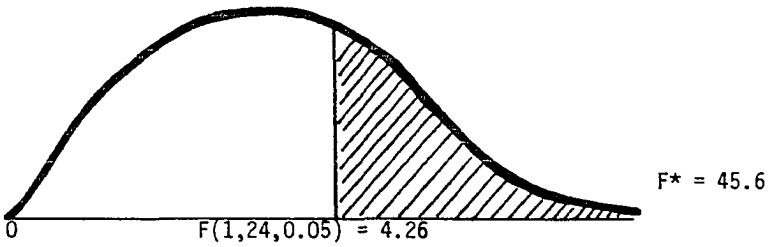
df(factor) = r-1 = 5
df(error)= r(c-1) = 24
df(total) = n-1 = 29

$$MS(FACTOR) = \frac{SS(FACTOR)}{df(factor)} = \frac{89{,}227}{5} = 17{,}845$$

$$MS(ERROR) = \frac{SS(ERROR)}{df(error)} = \frac{9{,}379}{24} = 391$$

$$F^* = \frac{MS(FACTOR)}{MS(ERROR)} = \frac{17{,}845}{391} = 45.6$$

$$F(5,24,0.05) = 3.90$$



Ho : $u_I = u_{II} = u_{III} = u_{IV} = u_V = u_{VI}$

Ha : $u_I \neq u_{II} \neq u_{III} \neq u_{IV} \neq u_V \neq u_{VI}$

$= 0.05$

df(numerator) = 5 df(denominator) = 24

Decision: Reject the null hypothesis since F* lies in the critical region.

Conclusion: The data show that there is considerable evidence that the treatment levels are significantly different at the 0.05 confidence level.

$$\Sigma Mu = u_4 - \frac{1}{5}u_1 - \frac{1}{5}u_2 - \frac{1}{5}u_3 - \frac{1}{5}u_5 - \frac{1}{5}u_6$$

Ho : $5u_4 = u_1 + u_2 + u_3 + u_5 + u_6$

Ha : $5u_4 \neq u_1 + u_2 + u_3 + u_5 + u_6$

$$Q1^2 = \frac{(5T_4-T_1-T_2-T_3-T_5-T_6)^2}{5(S^2+(-1)^2+(-1)^2+(-1)^2+(-1)^2+(-1)^2)}$$

$$= \frac{(5(259)-(1027)-702-913-1035-616)^2}{5(30)}$$

$$= 14980$$

$$F = Q^2{}_1/S^{1/2} = \frac{14980}{391}$$

$$F^* = 38.31$$

$F(1,24,0.05) = 4.26$

Decision: Reject the null hypothesis since F* lies in the critical region.

Conclusion: The data show that there is considerable evidence that Treatment Method IV is significantly different from all other treatment methods at the 0.05 confidence level.

$\Sigma Mu = u_4 - u_6 = 0$

$Ho : u_4 = u_6$

$Ha : u_4 \neq u_1$

$$Q^2_1 = \frac{(T_4 - T_6)^2}{5(S^2 \div (-1)^2)}$$

$$= \frac{(259-616)^2}{130}$$

$$= 980$$

$$F = Q^2_1 / S^{1/2} = \frac{980}{391}$$

$F^* = 2.51$

$F(1,24,0.05) = 4.26$

Decision: Fail to reject the null hypothesis since the F* value lies in the acceptable region.

Conclusion: The data show there is no significant difference between Treatment Methods IV and VI at the 0.05 confidence level.

The final conclusion from this AOV is that, since treatments IV and VI are equally efficient in TTHM removal, Method IV used a cheaper coagulant aid than Method VI with all other variables remaining constant between the two treatments. Therefore, the choice of Method IV is based on economic considerations.

Regression Analysis

Table 8 shows the projected annual TTHM means for water treatment facilities monitored in this study. Review of the tabulated results demonstrates what was both observed and what might logically be expected to occur. The estimated value of the Lawton plant July-September quarter was 62 ppb with the pilot study value being 54 ppb. Upon examining data presented in Table 8, an estimated annual TTHM mean of 22 ppb was determined for the Lawton Facility.

Table 8 further shows that implementation of Treatment Method IV utilized at the Lawton Medicine Park Water Treatment Plant would reduce annual TTHM means to well below the 100 ppb annual mean standard at every water treatment facility monitored in this study. It is important to note that this annual mean reduction can be accomplished by the use of Treatment Method IV during the critical quarter alone. This should be regarded as an observation and not a recommendation, however. A facility such as Sand Springs which shows TTHM values above the 100 ppb level in ever quarter should be judicious in implementing a single quarter alternative method. A facility such as Lawton, however, whose TTHM levels are well below the 100 ppb standard during three of the four quarters might consider the economic advantage of single quarter alteration. Table 9 shows data used in the following calculations:

$$r = \frac{n(\Sigma xy)-(\Sigma x)(\Sigma y)}{(n(\Sigma x^2)-(\Sigma x)^2)^{1/2}(n(\Sigma y^2)-(\Sigma y)^2)^{1/2}}$$

Table 8. **Projected Annual TTHM Means for Water Treatment Facilities Using e As the Correction Factor For $\hat{y}$**

Facility	.025x	$\pm$ e	$\hat{y} \pm e$
Altus	28	+28	56
Ardmore	22	+13	35
Bartlesville	58	+10	68
Broken Arrow	52	+8	60
Chickasha	45	-20	25
Claremore	37	-6	31
Clinton	37	+26	63
Del City	53	-11	42
Duncan	43	+20	63
Durant	14	+26	40
Guthrie	75	-6	69
Lawton	62	-40	22
McAlester	73	-27	46
Midwest City	29	+14	43
Muskogee	80	-22	58
Norman	56	-4	52
Oklahoma City-Draper	32	+7	39
Oklahoma City-Hefner	40	-8	32
OSU-Stillwater	33	-16	17
Okmulgee	34	-10	24
O.O.W.A.	18	+17	35
Ponca City	18	-5	13
P.V.I.A.	57	-15	42
Sand Springs	71	+19	80
Shawnee	42	+10	52
Tulsa-Jewell	33	-3	30
Tulsa-Mohawk	13	-3	10

$e = y_o - \hat{y}$

Regression Analysis

Table 9. TTHM Quarterly, Annual Means, and Computations

Facility	July-Sept (x)	Annual Mean (y)	x^2	y^2	xy
Altus	113	92	12769	8464	10396
Ardmore	89	64	7921	4096	5696
Bartlesville	231	137	53361	18769	31647
Broken Arrow	207	122	42849	14884	25254
Chickasha	179	80	32041	6400	14320
Claremore	147	77	21609	5929	11319
Clinton	147	108	21609	11664	15876
Del City	211	107	44521	11449	22577
Duncan	173	116	29929	13456	20068
Durant	54	58	2916	3364	3132
Guthrie	298	158	88804	24964	47084
Lawton	249	97	62001	9409	24153
McAlester	291	133	84681	17689	38703
Midwest City	114	78	12996	6084	8892
Muskogee	319	154	101761	23716	49126
Norman	225	121	50625	14641	27225
Oklahoma City-Draper	127	78	16129	6084	9906
Oklahoma City-Hefner	159	81	25281	6561	12879
OSU-Stillwater	132	59	17424	3481	7788
Okmulgee	136	67	18496	4489	9112
O.O.W.A.	72	59	5184	3481	4248
Ponca City	73	37	5329	1369	2701
P.V.I.A.	227	111	51529	12321	25197
Sand Springs	284	175	80656	30625	49700
Shawnee	169	105	28561	11025	17745
Tulsa-Jewell	132	71	17424	5041	9372
Tulsa-Mohawk	50	27	2500	729	1350
TOTAL	4608	2572	938,906	280,184	505,466

n = 27

$$r = \frac{27(505,466)-(4608)(2572)}{(27(938,906)-(4608)^2)^{1/2}(27(280,184)-(2572)^2)^{1/2}}$$

$= 0.91$

The decision point for n=27 is $\pm$ 0.381. Therefore, there is evidence of a linear correlation represented by the value of Pearson's product moment r of 0.91. A cause-effect relationship is implied in that a number of researchers have determined a direct relationship between TTHM formation and ambient water temperature.

The method of least squares is utilized to estimate the equation of the line of best fit where:

$y = b_0 + b_1x$ $\quad b_0$ = y-intercept $\quad b_1$ = slope

$$b_1 = \frac{n(\Sigma xy) - (\Sigma x)(\Sigma y)}{n(\Sigma x^2) - (\Sigma x)^2}$$

$$= \frac{27(505466)-(4608)(2572)}{27(938906)-(4608)^2}$$

$$= \frac{1,795,806}{4,116,798}$$

$= 0.44$

$b_0 = \bar{y} - b_1\bar{x}$ $\quad$ where $\bar{y} = \frac{y}{n} = \frac{2572}{27} = 95.26$

and $\bar{x} = \frac{x}{n} = \frac{4608}{27} = 170.67$

$= 95.26 - (0.44)(170.67)$

$= 20.2$

$\hat{y} = 20.2 + 0.44x$

In order to determine whether x, the quarterly value observed during July-September can be used to predict the value of y, the annual TTHM mean, a hypothesis test is utilized setting the y-intercept of the population equal to zero and using the t test to evaluate the acceptability of prediction.

H_o: $\beta_1 = 0$

H_a: $\beta_1 \neq 0$

df = n-2 = 25; α = 0.05; t(25,0.05) = 1.71

$$t = \frac{b_1 - \beta_1}{S_{b_1}}$$

where $S^2_{b_1}$ is an estimation of the variance among the calculated slopes (i.e. b_1s).

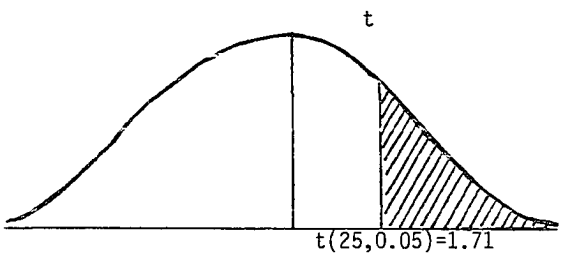
$$S^2_{b_1} = \frac{n(S^2_e)}{n(\Sigma x^2)-(\Sigma x)^2} = \frac{27(23.86)}{27(938,906)-(4608)^2}$$

$$= \frac{644.22}{4,116,798}$$

$$= 1.6 \times 10^{-4}$$

$$t = \frac{0.54 - 0}{(1.6 \times 10^{-4})^{1/2}}$$

$t^* = 34.79$



$t^* = 34.79$

Decision: The null hypothesis, H_0, is rejected since t* is in the critical region.

Conclusion: The slope of the line of best fit is greater than zero. There is evidence that a linear relationship exists between the two variables and that the annual TTHM mean for water treatment facilities can be predicted based on values of TTHMs empirically observed during the July-September sampling quarter.

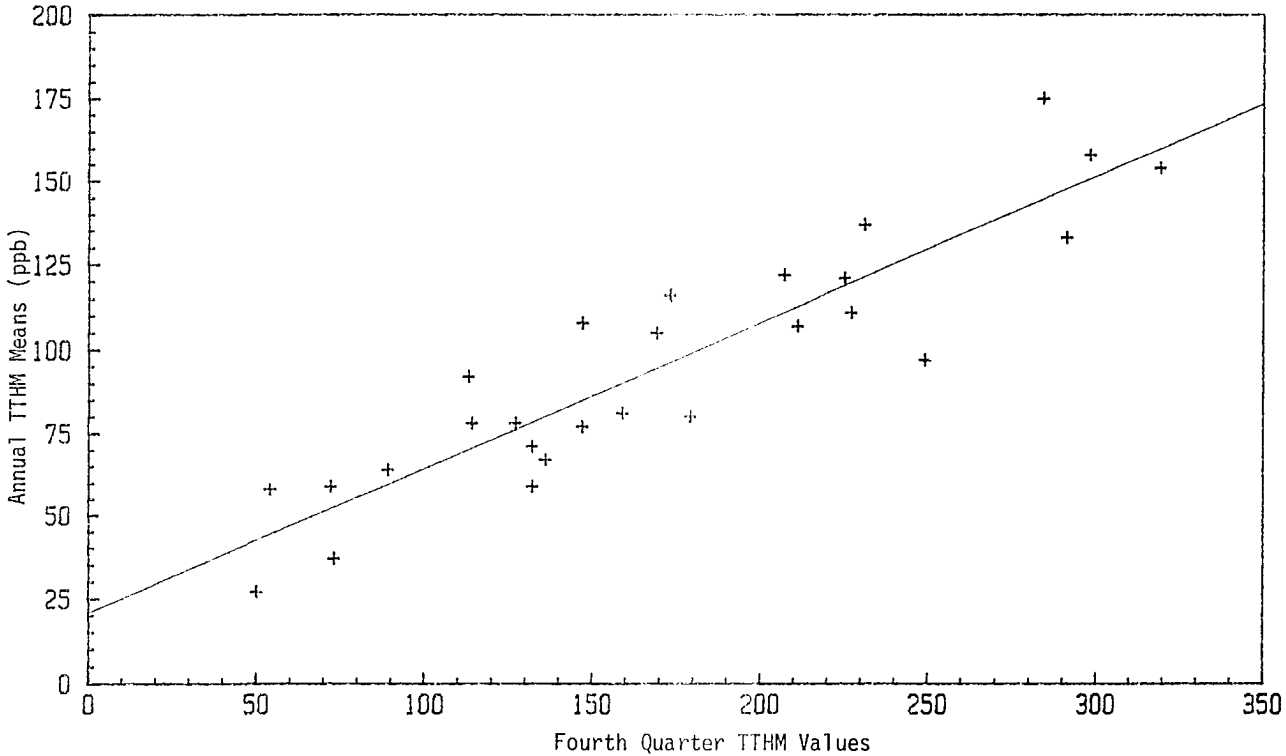
The confidence interval is given by:

$$b_1 \pm t(n-2,\ 0.025)(S_{b_1})$$
$$0.44 \pm (2.06)(1.6 \times 10^{-4})^{1/2}$$
$$0.44 \pm 0.03$$
$$0.41 \text{ to } 0.47$$

Therefore, the slope of the line of best fit of the population from which the sample was drawn is between 0.41 and 0.47 with 95% confidence. The line of best fit is shown in Figure 10.

The linear model $\hat{y} = 20.2 + 0.44x$ was used to calculate annual mean TTHM levels for the 27 Oklahoma water treatment facilities monitored in this study. In that Treatment Method IV demonstrated a 75% reduction in TTHMs during the critical period of the water year,

Figure 10. Linear Regression Plot of Annual TTHM Means vs. Critical Period Values



the value of x used in the model is adjusted to reflect this 75% reduction in order to predict annual mean TTHM values based on this percent reduction. In that $\hat{y}$ represents the best point estimate for each value of x, it is necessary to calculate confidence intervals for each value of y and construct confidence belts for x_0.

$\hat{y} = 20.2 + 0.44x$ where x is the adjusted value (25%) of the observed critical period TTHM value.

It would be repetitive to show all calculations of $\hat{y}$ for the 27 facilities. One, the Lawton facility $\hat{y}$ is calculated for illustrative purposes.

Lawton facility $x_0 = 249$ $0.25x = 62.25$

$\hat{y} = 20.2 + 0.44(62.25)$

$= 48$

The confidence interval for this calculated value of x is given by:

$$y \pm t(n-2, \alpha/2)(S_e^2)(1 + \frac{1}{n} + \frac{n(x_0 - \bar{x})}{n(\Sigma x^2)-(\Sigma x)^2})^{1/2}$$

The term S_e represents the deviation of the error about the regression line which is derived from the variance S_e^2.

The variance of the error e about the regression line is given by:

$$S_e^2 = \frac{SSE}{n-2} = \frac{(\Sigma y2)-(b_0)(\Sigma y)-(b_1)(\Sigma xy)}{n-2}$$

where S_e^2 is an estimate of the variance of the experimental error e and SSE is the sum of squares for error.

$$S_e^2 = \frac{(280,184)-(2.58)(2572)-(0.54)(505,466)}{25}$$

$$= \frac{596.6}{25}$$

$$= 23.86$$

$$S_e = (23.86)^{1/2} \qquad \text{and } t(n-2, \alpha/2) = t(25, 0.025)$$

$$= 4.88 \qquad = 2.06$$

$$\text{and } \bar{x} = 171$$

Therefore, the confidence interval for the calculated x for the Lawton Facility is:

$$48 \pm (2.06)(4.88)\left(1 + 1/27 + \frac{27(249-171)^2}{27(938,906) - (4608)^2}\right)^{1/2}$$

$$48 \pm (10.05)\left(1.037 + \frac{164,268}{25,350,462 - 21,233,664}\right)^{1/2}$$

$$48 \pm (10.05)\left(1.037 + \frac{164,268}{4,116,798}\right)^{1/2}$$

$$48 \pm (10.05)(1.037 + 0.04)^{1/2}$$

$$48 \pm (10.05)(1.038)$$

$$48 \pm (10.4) = 38 \text{ to } 58$$

The confidence interval for $\hat{y}_{x_0}$=249 is 38 to 58 at the 95% confidence level. In more pertinent terms, the linear model predicts that the annual mean TTHM value for the Lawton Facility, using prechloramination and optimized coagulation-sedimentation (Method IV), is not anticipated to exceed 58 ppb with 95% confidence. Empirically, the observed mean value of 54 ppb at the Lawton facility using Treatment Method IV (Table 4) during the period of peak TTHM production appears to substantiate this prediction.

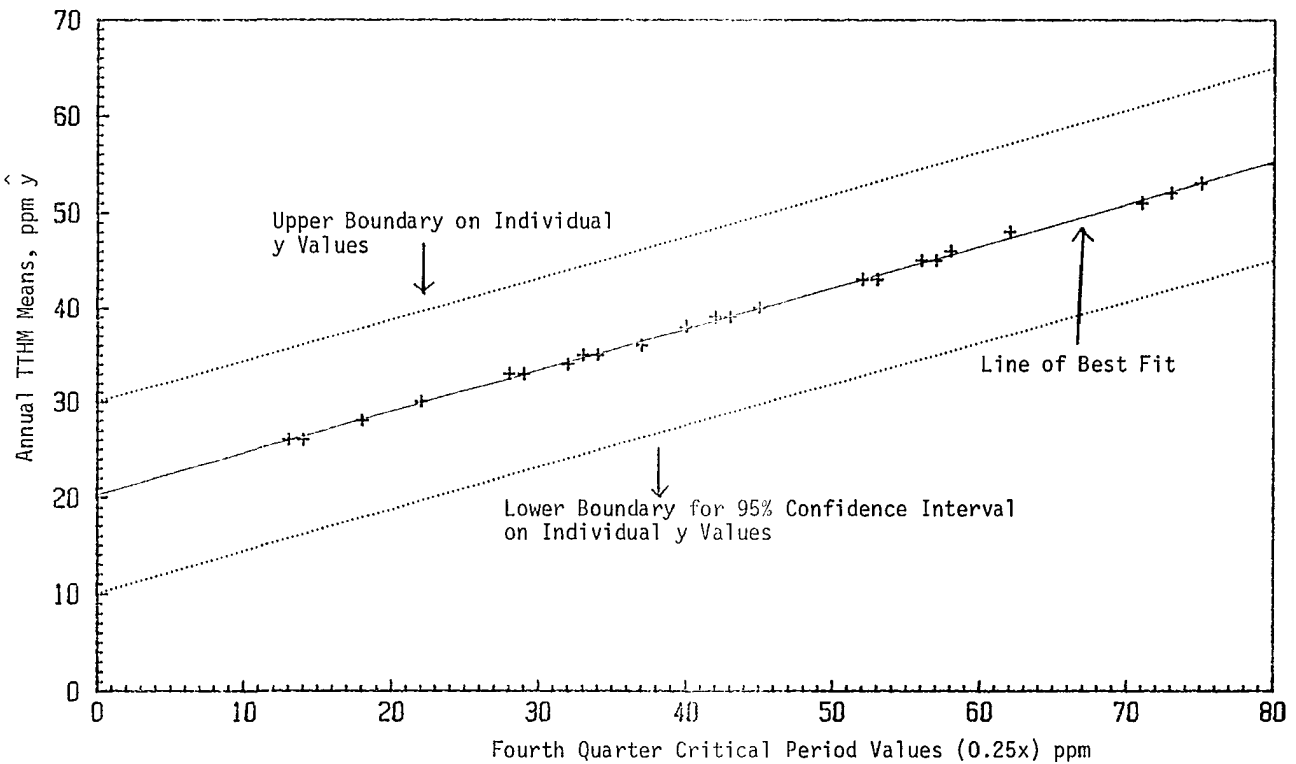
The above calculations were performed on the remaining 25 water treatment facilities monitored and are presented in Table 10. Calculations of the linear model and upper boundary of the interval estimate shown in Table 10 indicate that of the 27 Oklahoma public water supplies monitored in this study, 100% would be expected to meet the 100 ppb TTHM MCL by use of prechloramination and optimized coagulation.

The line of best fit with confidence intervals for these data is shown in Figure 11.

Table 10. Predicted Annual TTHM Means With Confidence Intervals

Facility	$\hat{y}$	Confidence Interval (95%)	Predicted Maximum Annual TTHM Mean
Altus	33	23 to 43	43
Ardmore	30	19 to 41	41
Bartlesville	46	36 to 56	56
Broken Arrow	43	33 to 53	53
Chickasha	40	29 to 51	51
Claremore	36	25 to 47	47
Clinton	36	26 to 46	46
Del City	43	33 to 53	53
Duncan	39	28 to 50	50
Durant	26	15 to 37	37
Guthrie	53	43 to 63	63
Lawton	48	38 to 58	58
McAlester	52	42 to 62	62
Midwest City	33	22 to 44	44
Muskogee	55	45 to 65	65
Norman	45	35 to 55	55
OKC-Draper	34	23 to 45	45
OKC-Hefner	38	28 to 48	48
OSU-Stillwater	35	24 to 46	46
Okmulgee	35	24 to 46	46
O.O.W.A.	28	16 to 40	40
Ponca City	28	16 to 40	40
P.V.I.A.	45	35 to 55	55
Sand Springs	51	41 to 61	61
Shawnee	39	29 to 49	49
Tulsa-A. B. Jewell	35	24 to 46	46
Tulsa-Mohawk	26	15 to 37	37

Figure 11. Confidence Belts for Y_{x_0}



CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

This project has demonstrated that the use of in-plant chloramination and optimization of coagulation aids can significantly reduce the production of trihalomethanes in the finished drinking water of the facility studied. Statistical analysis has shown that since this reduction during critical periods when ambient temperatures are highest (mid-summer) and when precursors from decaying vegetation are concurrently high, observed reductions of approximately 75% can be used to make reasonably accurate predictions as to the effect on the annual mean TTHM levels in finished water. There is good evidence that this alternative treatment method would achieve an annual mean TTHM level which is well below the maximum contaminant level allowed by the Safe Drinking Water Act.

Regression analysis using trihalomethane data from 27 surface water treatment plants in Oklahoma provided a linear model which showed

a correlation coefficient of 0.91 between the levels of TTHMs during critical periods and end-of-year annual TTHM means. Adjustment of critical period TTHM values for these facilities to a 75% reduction, followed by use of the linear model and an experimental error term correction indicated that the use of this treatment methodology would reduce annual mean TTHM levels at all 27 facilities to well below the TTHM standard. In that these annual mean predictions were based solely on critical period reduction of TTHM production, a considerable safety margin would be provided if this treatment method were used on a year-round basis. Even though the experimental error correction term may have shown an upper boundary for many facilities, the characteristic of the error term is to define deviations about the line of best fit. Therefore, those facilities with a negative error correction may have shown a lower boundary although this is not, in a statistical sense, the expectation. It would be unrealistic to conclude that the linear model and/or the level of percent reduction observed during this pilot study is precise enough to allow utilization of the recommended treatment alternative only during critical periods of the year. The study has shown, however, that there is strong evidence that the treatment alternative recommended, if used throughout the year, can be expected to reduce annual mean TTHM levels to below the 100 ppb standard.

Recommendations

Any water treatment facility desiring to implement the alternative treatment method recommended by this study should take into

account a number of factors:

Optimization of Coagulation-Sedimentation. This study in no way means to imply that other treatment facilities should alter coagulant aids currently in use and certainly does not imply that the optimum dose determined for the Lawton facility will be the same for other facilities. It is recommended that coagulant aids currently in use be frequently jar-tested in order to determine optimum coagulation-sedimentation. Naturally, due to changes in the characteristics of raw water throughout the year, optimum dosage rates will fluctuate considerably. These fluctuations will be particularly observable from spring through late summer.

Utilization of Pre-chloramination. Ideally, ammonium sulfate should be added upstream of the chlorination point. The resulting formation of chloramines is likely just as effective for pre-disinfection if the ammonium sulfate slurry is added downstream, although there are conflicting opinions regarding which should be added first. It should be borne in mind that combined chlorine residuals require longer contact time (one to four hours) for adequate disinfection than do free chlorine residuals. The optimum dose of ammonium sulfate and chlorine gas should be derived from a 1:1 molar ratio in order to preclude break-point chlorination with the subsequent formation of free chlorine residuals and enhanced TTHM formation.

Adjustment of pH. In that the reaction rate of chlorine with ammonium sulfate to produce chloramines is most rapid at a pH of 8.3, the addition of slaked lime should be adjusted to produce this pH as closely as possible. Lowering the pH has the added benefit of further reducing TTHM formation. However, caution should be exercised to avoid delivering corrosive water to the distribution system. A Total Alkalinity of 75-100 ppm should be maintained to avoid corrosivity of finished water at this pH and to assure delivery of soft water.

Disinfectant Residuals and Bacteriological Quality. It is of particular importance to maintain a bacterial barrier in light of the fact that disinfectant modifications, both in reduction of contact time and use of chloramines during in-plant treatment, could have a significant effect on chlorine residual maintenance throughout the distribution system. Standard plate counts should be determined twice per month to gather information on any changes in quality in the system. These should be taken at not less than four points in the distribution system. Particular attention should be applied to dead-end lines and the most distant points in the distribution system.

Treatment Contingencies. Substituting a combined chlorine residual for a free chlorine residual can cause considerable alterations in overall treatment efficiency. Free chlorine is not only a powerful disinfectant, but may also serve as a coagulation-clarification aid, oxidize iron and manganese, destroy tastes and

odors, remove color, and prevent algae and bacterial slime growths in filters and treatment units. In the event that the aforementioned alternatives are implemented, plant operations may become more difficult in that coagulation might be more difficult, tastes and odor problems will be more difficult to control, and the build-up of algae and bacterial slimes in both the clarification basis and filters will be more rapid. Shock-chlorination for brief periods can alleviate these conditions to some degree, but only close vigilance of coagulation efficiency and the quality of finished water can assure continuous delivery of the highest quality of water to consumers. The plant operator should be prepared to increase coagulation-aid feeds in the event that poor flocculation occurs and to resume pre-chlorination for brief periods in the event of rapid filter head-loss, build-up of slime layers in clarification basins, or taste and odor problems.

Figures 12 and 13 illustrate the relative costs of utilizing chlorine, ozone, chlorine dioxide, and chloramines as disinfectants and the operational costs associated with using GAC and PAC.

Figure 12. Relative Cost of Disinfectants (EPA)

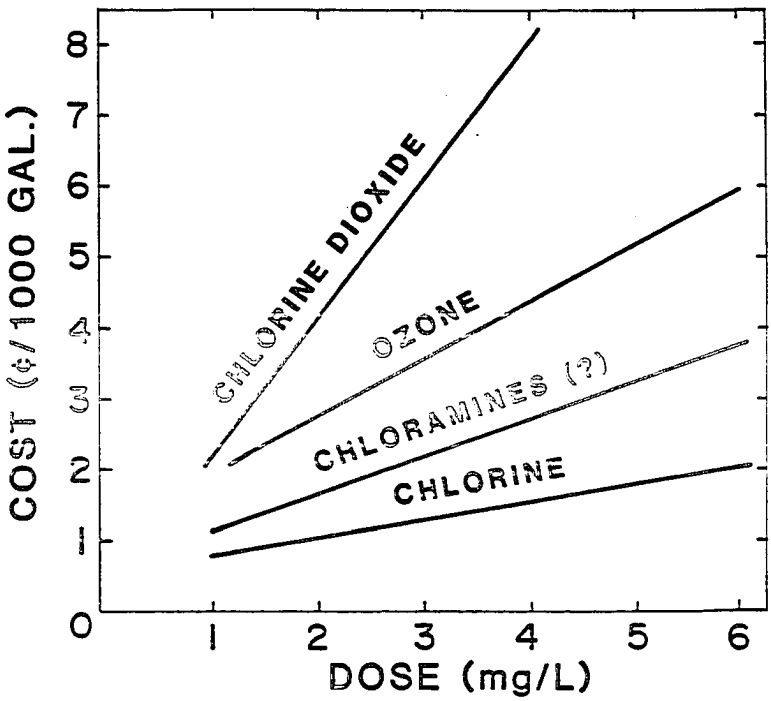
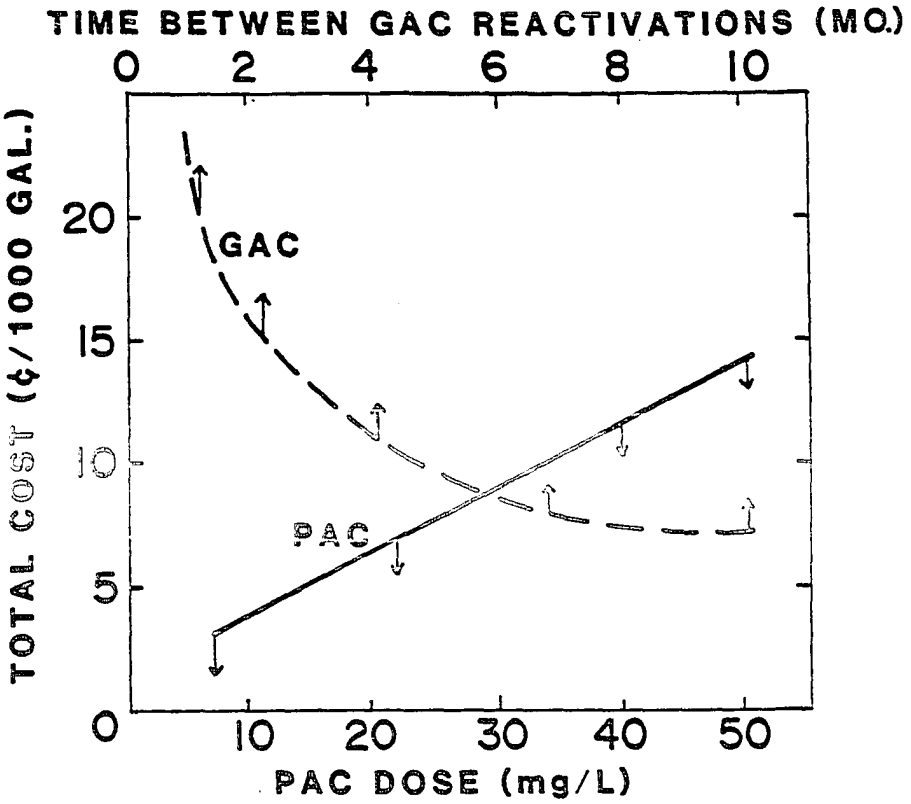


Figure 13. Cost of PAC and GAC Treatment (EPA)



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APPENDIX

Table A-1. Chlorination Practices and Types of Water Treatment.

Facility	County	Prechlorination	Disinfectant	Remarks
Adair	Mayes	no	Chlorine Gas	Coag, SS Filt, TO-Carbon
Alberta Creek Resort	Marshall	yes	Chlorine Gas	Coag, SS Filt
Altus	Jackson	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr, Soft
Anadarko	Caddo	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr, Soft
Antlers	Pushmataha	yes	Chlorine Gas	Coag, Sed, SS Filter, Corr, Soft
Ardmore	Carter	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr, TO-C
Ardmore Air Park	Carter	yes	Chlorine Dioxide	Coag, Sed, SS Filt, Corr
Atoka	Atoka	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Corr
Avant Utility Authority	Osage	no	Sodium Hypochlorite	Coag, Sed, SS Filt, Corr
Barnsdall	Osage	no	Chlorine Gas	Coag, Sed, RS Filt, Corr
Bartlesville	Washington	unknown	Unknown	Coag, Sed, Filt
Beavers Bend State Park	McCurtain	no	Chlorine Gas	Coag, Sed, Dual Filt
Beggs	Okmulgee	yes	Chlorine Gas	Coag, RS Filt, Corr
Bixby	Tulsa	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr, TO-C
Blackwell	Kay	yes	Chlorine Gas	Coag, Sed, RS Filt, Soft
Boynton	Muskogee	no	Calcium Hypochlorite	Coag, Filt, Soft
Bridgeview Resort	Marshall	no	Chlorine Dioxide	Coag, SS Filt
Bristow Point	Pittsburg	yes	Unknown	Coag, Sed, SS Filt, Corr
Broken Arrow	Tulsa	yes	Chlorine Dioxide	Coag, Anth Filt, Corr, Soft, TO-C
Broken Bow	McCurtain	yes	Chlorine Gas	Coag, Sed, SS Filt, Corr, Soft
Chandler	Lincoln	no	Unknown	Coag, Sed, Filt, TO
Checotah	McIntosh	no	Chlorine Gas	Coag, Sed, Mixed Filt
Chelsea	Rogers	yes	Chlorine Gas	Coag, Sed
Cherokee Land Yacht	Cherokee	no	Unknown	Unknown
Cherokee Landing	Cherokee	no	Calcium Hypochlorite	Coag, Sed, SS Filt
Cheyenne	Roger Mills	no	Chlorine Gas	Coag, SS Filt, Corr, Soft
Chickasha	Grady	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr, Soft, TO
Claremore	Rogers	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Soft, Fe-K
Clayton PWA	Pushmataha	yes	Chlorine Gas	Coag, Sed, SS Filt, Corr, Soft
Cleveland	Pawnee	no	Unknown	Coag
Clinton	Custer	yes	Chlorine Gas	Coag, Sed, Anth Filt, TO-C
Coalgate PWA	Coal	yes	Chlorine Gas	Unknown
Collinsville	Tulsa	yes	Unknown	Coag, Sed, RS Filt, Corr
Cookson Bend Resort	Cherokee	no	Sodium Hypochlorite	Coag, Sed, SS Filt

Table A-1. (cont.)

Facility	County	Prechlorination	Disinfectant	Remarks
Cookson Village TP	Cherokee	no	Sodium Hypochlorite	SS Filt, Corr
Cookson Water and Dev Co.	Cherokee	no	Calcium Hypochlorite	Coag, Sed, Press Filt, Corr
Coweta	Wagoner	no	Chlorine Gas	Coag, Anth Filt, Soft, TO-C
Creek County RWD # 1	Creek	yes	Sodium Hypochlorite	Coag, Sed, RS Filt, Corr
Creek County RWD # 7	Creek	yes	Calcium Hypochlorite	Coag, RS Filt, Corr
Cushing	Payne	no	Chlorine Gas	Coag, Sed, RS Filt, Corr, Soft
Davenport	Lincoln	no	Unknown	Coag, Sed, RS Filt, Corr, Soft, TO-C
Davis	Murray	yes	Chlorine Gas	Coag, Sed, SS Filt, Soft
Del City	Oklahoma	yes	Chlorine Gas	Coag, GAC Filt, Corr, TO
Delaware	Nowata	no	Chlorine Gas	Coag, Sed, RS Filt, Soft, TO-K
Disney RWD # 3	Mayes	no	Unknown	Unknown
Dougherty	Murray	unknown	Unknown	Coag, Sed, Filt
Duncan	Stephens	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr-C, Soft
Durant	Bryan	no	Chlorine Gas	Coag, Sed, RS Filt, Corr, TO-C
Dustin	Hughes	no	Chlorine Gas	Coag, Sed, RS Filt, Corr
East Central Oklahoma Water	Sequoyah	no	Unknown	Unknown
Elmore City	Garvin	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
Eufaula	McIntosh	yes	Chlorine Gas	Coag, Sed, Filt, Corr
Fairfax	Osage	no	Chlorine Gas	Unknown
Fort Gibson	Muskogee	no	Chlorine Gas	Coag, Anth Filt
Foss Reservoir MCD	Custer	yes	Chlorine Gas	Coag, Clarif, Anth Filt
Frederick	Tillman	yes	Chlorine Gas	Coag, Anth Filt, Corr, TO-C
Goddard Youth Camp	Murray	unknown	Unknown	Unknown
Grand Lake Towne	Mayes	no	Sodium Hypochlorite	SS Filt
Grand Tara	Delaware	no	Calcium Hypochlorite	Coag, Sed, SS Filt
Grove MSA	Delaware	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr
Gull Bay Water System	Osage	yes	Calcium Hypochlorite	Coag, Sed, SS Filt, Corr
Guthrie	Logan	yes	Unknown	Coag, Sed, Filt, Corr
Haskell County Water Co.	Haskell	yes	Chlorine Gas	Coag, Sed, SS Filt, Corr
Heavener	LeFlore	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
Henryetta	Okmulgee	no	Chlorine Gas	Coag, Sed, Anth Filt, Soft
Hickory Hills	Hughes	no	Calcium Hypochlorite	Coag, Sed, SS Filt
Hobart	Kiowa	no	Unknown	Coag, Sed, Anth Filt, Corr, Soft
Holdenville	Hughes	yes	Chlorine Gas	Coag, Sed, Dual Filt, Corr

Table A-1. (cont.)

Facility	County	Prechlorination	Disinfectant	Remarks
Hominy	Osage	no	Chlorine Gas	Coag, Sed, RS Filt, Corr, Soft, Aer
Hugo	Choctaw	unknown	Unknown	Unknown
Hulbert PWA	Cherokee	no	Chlorine Gas	Coag, Mixed Filt, Corr
Hunters Cove	Mayes	unknown	Unknown	Unknown
Idabel	McCurtain	yes	Chlorine Gas	Coag, Sed, SS Filt, Corr, Soft
Jay	Delaware	yes	Chlorine Gas	Sed, Anth Filt
Keota		no	Chlorine Gas	Coag, Sed, RS Filt, Corr, TO-C
Ketchum PWA	Craig	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr
Keys RWD # 2	Cherokee	no	Unknown	Sed, Filt
Kiowa	Pittsburg	unknown	Chlorine Gas	Coag, Anth Filt, Corr
Krebs	Pittsburg	no	Chlorine Dioxide	Coag, Sed, RS Filt, Corr
Lake Crest Prop	Wagoner	yes	Unknown	Unknown
Lakeview Water Co. Inc.	Cherokee	yes	Unknown	Coag, Sed, RS Filt
Lakewood Utility Inc.	Cherokee	no	Calcium Hypochlorite	Sed, SS Filt
Langley	Mayes	yes	Calcium Hypochlorite	Coag, Sed, RS Filt, Corr
Langston University	Logan	yes	Unknown	Unknown
Lawton	Comanche	yes	Chlorine Gas	Coag, Sed, Anth Filt, Soft, Amm
Lenopah	Nowata	no	Chlorine Gas	Coag, Sed, RS Filt, Corr, TO-K
Lincoln County RWD # 1	Lincoln	yes	Calcium Hypochlorite	Coag, Sed, RS Filt, Corr
Little Glasses Resort	Marshall	no	Chlorine Dioxide	Coag, Sed, SS Filt
Locust Grove	Mayes	yes	Chlorine gas	Coag, RS Filt
Lucien RWD # 1	Noble	yes	Chlorine Gas	Coag, Sed, RS Filt
Madill	Marshall	yes	Chlorine Gas	Coag, Anth Filt, Soft
Mannford	Creek	yes	Chlorine Gas	Coag, RS Filt, Corr, Soft
Marshall	Logan	unknown	Unknown	Unknown
Marshall County Water Co.	Marshall	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Corr
Mason Oaks RWD # 3	Haskell	unknown	Unknown	Unknown
Mayes County RWD # 6	Mayes	yes	Calcium Hypochlorite	Coag, Sed, RS Filt
Maysville	Garvin	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
McAlester	Pittsburg	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
McCurtain County RWD # 1	McCurtain	yes	Chlorine Gas	Coag, Sed, SS Filt, Soft
Meeker	Lincoln	unknown	Unknown	Coag, Mixed Filt, Corr, Soft
Midwest City	Oklahoma	yes	Chlorine Gas	Coag, Anth Filt, Corr, TO-C
Monkey Island EB	Delaware	no	Sodium Hypochlorite	Coag, Press Filt

Table A-1. (cont.)

Facility	County	Prechlorination	Disinfectant	Remarks
Mountain Fork RWD # 3	McCurtain	yes	Chlorine Gas	Coag, Sed, SS Filt, Corr, Soft
Muldrow	Sequoyah	no	Calcium Hypochlorite	Coag, SS Filt
Murray State College	Johnston	yes	Chlorine Gas	Coag, Sed, Press Filt, Corr
Muskogee	Muskogee	yes	Chlorine Gas	Coag, Dual Filt, Corr, Soft
Muskogee County RWD # 3	Muskogee	no	Calcium Hypochlorite	Coag, Anth Filt, Corr
Norman	Cleveland	yes	Chlorine Gas	Coag, Anth Filt, Corr, Soft, TO
Norwood RWD # 1	Cherokee	yes	Calcium Hypochlorite	Coag, Sed, Anth Filt, Corr
Nowata	Nowata	no	Chlorine Gas	Coag, Sed, RS Filt, Corr, Soft
Nowata RWD # 1	Nowata	yes	Chlorine Gas	Coag, Sed, Filt, Corr, TO-K
Okay PWA	Wagoner	no	Unknown	Coag, Sed, Filt
Oklahoma City Draper	Oklahoma	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr, TO-C
Oklahoma City Hefner	Oklahoma	yes	Chlorine Gas	Coag, Anth Filt, Corr, Aer
Oklahoma City Overholser	Oklahoma	yes	Chlorine Gas	Coag, Anth Filt, Corr, TO-C
Okemah Lake TP	Okfuskee	unknown	Unknown	Unknown
Okemah PWA	Okfuskee	no	Chlorine Gas	Coag, Mixed Filt, Corr
OOWA	Mayes	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Corr
Okmulgee	Okmulgee	yes	Chlorine Gas	Coag, Anth Filt, Corr, Soft
Oklahoma State University	Payne	yes	Chlorine Gas	Coag, Sed, Dual Filt, Corr
OUBS	Marshall	no	Chlorine Dioxide	Coag, Sed, SS Filt
Paradise Hill Inc.	Sequoyah	yes	Unknown	Unknown
Pauls Valley	Garvin	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr, Soft
Pawhuska	Osage	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
Pawnee	Pawnee	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
Perry	Noble	yes	Chlorine Gas	Coag, Sed, Anth Filt
Petit Mountain Water	Cherokee	no	Unknown	Unknown
Petit Bay Water Association	Cherokee	unknown	Unknown	Unknown
Pittsburg	Pittsburg	yes	Calcium Hypochlorite	Coag, SS Filt, Corr
Pittsburg County RWD # 4	Pittsburg	no	Calcium Hypochlorite	Coag, Sed, SS Filt, Corr
Pittsburg Water Authority	Pittsburg	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Corr, TO
Pittsburg PWA	Pittsburg	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
Ponca City	Kay	yes	Chlorine Gas	Coag, Sed, RS Filt, Stab
Port Duncan	Delaware	yes	Sodium Hypochlorite	Coag, RS Filt, Corr
Porum PWA	Muskogee	yes	Chlorine Gas	Coag, Anth Filt, Corr
PVIA	LeFlore	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Corr

Table A-1. (cont.)

Facility	County	Prechlorination	Disinfectant	Remarks
Red Oak	Latimer	no	Chlorine Gas	Coag, Sed, Mixed Filt, Corr
Robbers Cave State Park	Latimer	yes	Chlorine Dioxide	Coag, Sed, Anth Filt, Corr
Rogers County RWD # 3	Rogers	yes	Chlorine Gas	Coag, Sed, Filt, Soft, Fe-K
Rogers County RWD # 4	Rogers	yes	Chlorine Gas	Coag, Sed, Filt, Fe-K
Rogers County RWD # 5	Rogers	yes	Unknown	Coag, Sed, Filt, Soft
RWD # 1 Atoka County	Atoka	no	Chlorine Dioxide	Coag, Sed, Filt, Corr
Salina	Mayes	yes	Chlorine Gas	Coag, Sed, RS Filt
Sallisaw	Sequoyah	yes	Chlorine Gas	Coag, Sed, Anth Filt
Sand Springs	Tulsa	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
Sapulpa	Creek	yes	Chlorine Gas	Coag, Sed, Filt, Corr
Sequoyah County Wat Assoc	Sequoyah	yes	Chlorine Gas	Coag, Sed, Mixed Filt
Sequoyah SP Pk (main plant)	Cherokee	no	Calcium Hypochlorite	Coag, Sed, SS Filt
Shawnee	Paootwatomie	yes	Unknown	Coag, Sed, Filt
Sherwood Forest Addition	McIntosh	yes	Sodium Hypochlorite	Coag
Shidler	Osage	yes	Calcium Hypochlorite	Coag, Sed, Corr, Soft, TO-C
Shoreline Estates	Pittsburg	no	Chlorine Dioxide	Coag, Sed, SS Filt, Corr
Snyder	Kiowa	yes	Chlorine gas	Coag, Sed, Anth Filt, Corr, Soft
Soldier Creek	Marshall	no	Chlorine Dioxide	Coag, Sed, SS Filt
Southern Oklahoma Water Co.	Carter	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Corr
Spavinaw	Mayes	yes	Chlorine Gas	Coag, Sed, Press Filt
Spinnaker Point Resort	Delaware	no	Calcium Hypochlorite	Sed, SS Filt
Spiro	LeFlore	yes	Chlorine Gas	Coag, Mixed Filt, Corr
Sportsman Shores	Mayes	no	Calcium Hypochlorite	Sed, SS Filt
Spring Creek Water	Mayes	no	Calcium Hypochlorite	Sed, SS Filt
Stigler	Haskell	yes	Chlorine Gas	Coag, Sed, RS Filt, Corr
Stilwell	Adair	unknown	Chlorine Gas	Coag, Sed, SS Filt
Stringtown VO Training	Atoka	yes	Chlorine Gas	Coag, Sed, SS Filt, Corr
Stroud PWA	Lincoln	no	Chlorine Gas	Coag, TS Filt, Corr
Summitt Water Co.	Cherokee	unknown	Calcium Hypochlorite	Coag, Sed, Press Filt, Corr
Tahlequah	Cherokee	yes	Chlorine Gas	Coag, Sed, Anth Filt
Talihina	LeFlore	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Corr, Soft
Tecumseh	Pottowatomie	yes	Sodium Hyypochlorite	Coag, Sed, Anth Filt, Corr, Soft
Temple	Cotton	unknown	Chlorine Gas	Coag, Sed, RS Filt, Corr, TO-C
Tenkiller Water Co. (CC)	Cherokee	unknown	Unknown	Coag, Sed, Filt

Table A-1. (cont.)

Facility	County	Prechlorination	Disinfectant	Remarks
Tenkiller Water Co. (WP)	Cherokee	unknown	Unknown	Unknown
Tenkiller Shores West	Cherokee	unknown	Unknown	Unknown
Tenkiller State Park	Cherokee	no	Calcium Hypochlorite	Sed, SS Filt, Corr
Terapin Creek Club	Cherokee	unknown	Sodium Hypochlorite	Coag, Sed, SS Filt
Tishimingo	Johnston	yes	Chlorine Gas	Coag, Mixed Filt, Corr
Treasure Lake Job Corp.	Comanche	unknown	Unknown	Unknown
Tulsa Lynn Lane	Tulsa	yes	Chlorine Gas	Coag, Sed, Anth Filt, Corr
Tulsa Mowhawk	Tulsa	yes	Chlorine Gas	Coag, Sed, RS Filt
U.S. Army Ammunition Plant	Pittsburg	no	Chlorine Gas	Coag, Sed, Anth Filt, Corr
Valliant	McCurtain	yes	Chlorine Gas	Coag, Sed, SS Filt, Corr, Soft
Verden	Grady	yes	Sodium Hypochlorite	Coag, Sed, RS Filt
Vinita	Craig	unknown	Chlorine Gas	Coag, Sed, RS Filt, Corr
Wagoner	Wagoner	yes	Chlorine Gas	Coag, Anth Filt
Wagoner County RWD # 1	Wagoner	unknown	Unknown	Unknown
Wagoner County RWD # 2	Wagoner	unknown	Unknown	Unknown
Wagoner County RWD # 7	Wagoner	unknown	Unknown	Unknown
Walters	Cotton	no	Chlorine Gas	Coag, Sed, RS Filt, TO-C
Wapanucka PWA	Johnston	no	Chlorine Dioxide	Coag, RS Filt, Corr
Warner PWA	Muskogee	no	Chlorine Gas	Coag, Filt, Corr
Washington County RWD # 3	Washington	yes	Chlorine Gas	Coag, Anth Filt, Corr, Soft
Watts PWA	Adair	unknown	Unknown	Coag, GAC Filt, Corr, TO-C
Weleetka	Okfuskee	no	Chlorine Gas	Coag, Sed, RS Filt, Corr
Western Hills State Lodge	Cherokee	no	Chlorine Gas	Coag, Anth Filt
Wetern State Hospital	Woodward	yes	Chlorine Gas	Coag, Sed, Anth Filt, Soft
Wetumka	Hughes	no	Chlorine Gas	Coag, Sed, RS Filt, Corr
Wewoka Water Inc.	Seminole	yes	Chlorine Gas	Coag, Sed, RS Filter, Corr, TO-C
Wilburton	Latimer	yes	Chlorine Gas	Coag, Sed, Mixed Filt, Corr
Woodhaven Water Company	Cherokee	unknown	Calcium Hypochlorite	Coag, Sed, SS Filt
Wright City	McCurtain	yes	Chlorine Gas	Coag, Sed, SS Filt, Corr, Soft
Wynnewood	Garvin	yes	Chlorine Gas	Coag, RS Filt, Corr, Soft

Flow Diagram: Lawton Medicine Park Water Treatment Plant

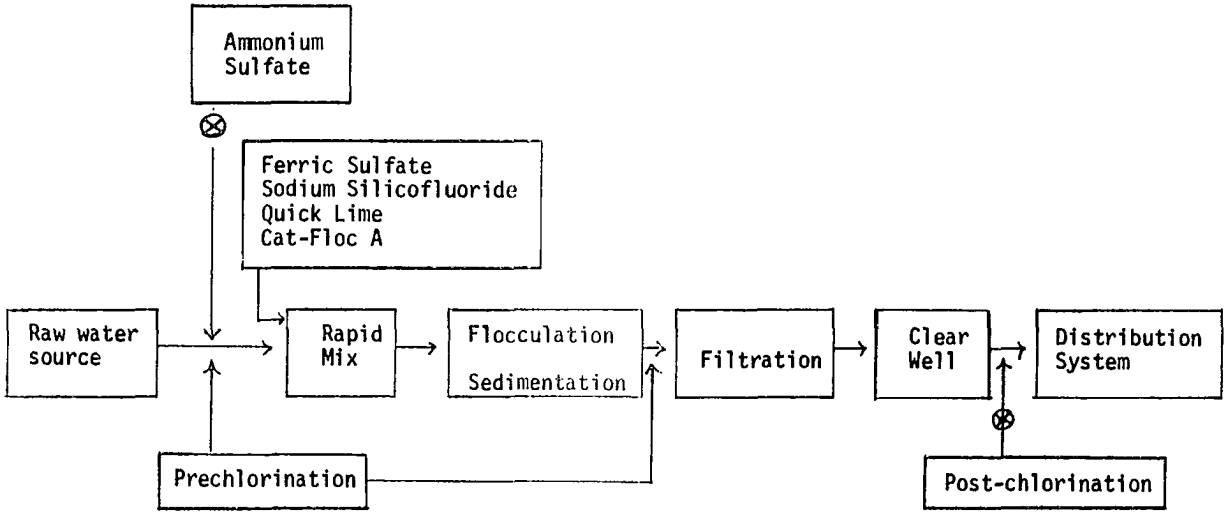

Table A-2. Lawton Raw Water Analysis; June 28, 1982

PARAMETER	UNITS	VALUE
Chloride	mg/L	24.0
Fluoride	mg/L	< 0.5
NO_3/NO_2-N	mg/L	14.3
pH	SU	6.7
Sulfate	mg/L	52.0
TDS	mg/L	324.0
Total Alkalinity	mg/L	142.0
Total Hardness	mg/L	180.0
Turbidity	NTU	12.0
NV Total Organic Carbon	mg/L	18.0
Color, Apparent	Color Units	20.0
*Arsenic	ug/L	< 10.0
Barium	ug/L	150.0
Cadmium	ug/L	< 2.0
Chromium	ug/L	< 10.0
Copper	ug/L	5.0
Iron	ug/L	160.0
Lead	ug/L	< 20.0
Manganese	ug/L	< 20.0
Mercury	ug/L	< 0.5
Selenium	ug/L	< 5.0
Silver	ug/L	< 3.0
Sodium	ug/L	42.0
Zinc	ug/L	12.0
Chlorinated Hydrocarbons, Total	ug/L	< 10.0

*All metals reported as Total